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Resume of Research activities of the
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EDITORIAL NOTE

Despite the fact that this University is completing its hundredth year since its inception, the older of the Science Departments are very much younger, having been in existence only for a quarter of a century. In presenting this résumé of the highlights of the investigations of the Science Departments of this University, we have much pleasure in dedicating this as our humble contribution to the progress of science and learning in the various Universities all over the world.

कर्मण्येवाधिकारस्ते मा फलेषु कदाचन।
मा कर्मफलहेतुर्भूर्मा ते सङ्गोऽस्त्वकर्मणि॥

Thy business is with action only, never with its fruits; so let not the fruit of action be thy motive, nor be thou to inaction attached.

—The immortal *Bhagavad Gita*, 2nd discourse, sloka 47.

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Department of Botany

1930 — 1956

The first Honorary Director, Professor T. Ekambaram initiated some amount of work in Botany and during the short period of his tenure of office, three theses and some publications appeared.

It was only in 1933 that Professor M. O. P. Iyengar took over as the first permanent Director and established a school of research in the field of Algae. The work initiated was broad based and covered limnological observations of fresh, estuarine and marine algal forms, systematics, life-histories, morphology and cytology. Much of this was pioneering work in so far as this country was concerned. In the field of limnology much of the work has been reviewed critically by Iyengar (1939) under the heads: lakes and larger pieces of water; algal flora of temporary waters and their succession; pieces of water with permanent water blooms caused by species of *Microcystis;* paddy field algae; algae of estuarine regions; algae in relation to aquatic animals; and algae and mosquito larvae.

In the field of systematics the major work has been on living and fossil diatoms (Venkataraman, 1939; Subrahmanyan, 1946; Iyengar and Subrahmanyan, 1943), desmids (Iyengar and Vimala Bai, 1941) and Cyanophyceae (Iyengar and Desikachary, 1944). Several new genera belonging to various groups of algae were also described: *Cladospongia* Iyengar and Ramanathan (1940) in the Craspedomonadaceae; *Characiosiphon* Iyengar (1936), *Pseudovalonia* Iyengar (1938), *Triplastrum* Iyengar and Ramanathan (1942), *Hormidiella* Iyengar and Kanthamma (1940), *Heterothricopsis* Iyengar and Kanthamma (1941) and *Gloeotilopsis* Iyengar and Philipose (1956) in the Chlorophyceae; *Chrysodictyon* Ramanathan (1946) in the Chrysophyceae; and *Mastigocladopsis* Iyengar and Desikachary (1946b), *Camptylonemopsis* Desikachary (1948) and *Iyengariella* Desikachary (1953) in the Cyanophyceae. Many new species and forms belonging to different groups were also described.

Life-history studies were carried out on a number of forms, notably in *Eudorina elegans* (Iyengar, 1937), *Pseudovalonia forbesii* (Iyengar, 1938), *Cylindrocapsa geminella* (Iyengar, 1939), *Caulerpa* (Iyengar, 1940), *Characiosiphon rivularis* (Iyengar,

1954), *Anadyomene stellata* (Iyengar and Ramanathan, 1940), *Microdictyon tenuius* (Iyengar and Ramanathan, 1941), *Cyclotella meneghiniana* (Iyengar and Subrahmanyan, 1942), *Characium terrestris* (Kanthamma, 1940), *Enteromorpha* (Ramanathan, 1936, 1939b), *Carteria* (Ramanathan, 1942), *Bacteriastrum* (Subrahmanyan, 1945a), *Navicula halophila* (Subrahmanyan, 1946b), etc. Life-history studies have also been carried out on several of the new genera already mentioned.

Another aspect on which much attention has been focussed is the developmental morphology and cytology of many tropical forms. Particular mention may be made here of the work on *Melobesia farinosa* (Balakrishnan, 1946), *Grateloupia lithophila* (Balakrishnan, 1949), *Eudorina indica* (Doraiswami, 1940), *Spirogyra* (Doraiswami, 1946), *Polysiphonia platycarpa* (Iyengar and Balakrishnan, 1950), *Enteromorpha compressa* var. *ligulata* (Ramanathan, 1939b), *Micrasterias denticulata* var. *notata* (Saraswathi, 1946), various species of diatoms (Subrahmanyan, 1945b, 1946b) and *Chara zeylanica* (Sundaralingam, 1946, 1954).

The outcome of all these carefully planned and precise scientific investigations has been one of enriching our knowledge of algae, and tropical algae in particular, in all its aspects: morphological, cytological, ecological, developmental and taxonomical. Indeed, much of this work on the green algae has been summarised by Professor Iyengar (1951) in a chapter on Chlorophyceae in the *Manual of Phycology* edited by Prof. G. M. Smith of the Stanford University and published by the Chronica Botanica Co.

In 1944 there was a re-orientation of the work from Algae to Mycology and Plant Pathology in the Department with the appointment of Professor T. S. Sadasivan as Director in succession to Professor M. O. P. Iyengar. Broadly speaking, the following investigations have been undertaken during the past twelve years: soil-borne diseases of plants (including micro-ecology of soil fungi and other microorganisms), the physiology of fungi and the physiology of host-parasite relationships, particularly Fusariose wilts in plants, techniques in bioassay and chromatography, spectrochemical studies on uptake of ions by plants, work on vivotoxins and fungal enzymes, respiration and electrophoretic studies in plant tissues, and systematics and taxonomy of fungi.

The work on soil conditions and root diseases, particularly those of cotton and pigeon pea, has been one of detailed studies

of survival of fungal pathogens in soils on the face of amendments and as affected by soil microfloras (Subramanian, 1946 a, b, 1950; Sarojini, 1950; Sulochana, 1952 a-d; Kovoor, 1954; Ramakrishnan, 1955a). It has been shown that *Fusarium vasinfectum,* the cotton wilt organism, is a *soil inhabitant* and *Fusarium udum,* the pigeon pea wilt fungus, is a *root inhabitant* and that the heavy metal zinc in pure culture controls the toxin (Fusaric acid) output of the former organism (Kalyanasundaram and Saraswathi-Devi, 1955a). This finding has found practical application in that the zinc content (as determined by bioassay using *Aspergillus niger*) of the major *Fusarium* wilt-sick cotton soils of Southern India is optimum for toxin production *in situ,* whereas a high concentration of zinc acts as a limiting factor in certain other areas where the fungus is present but is innocuous. The role of trace elements in the control of plant wilts, for which considerable evidence has accumulated, has been reviewed in detail (Sadasivan, 1950, 1951, 1952; Sadasivan and Subramanian, 1954a). Microbial antagonism in soils as another factor in the delimitation of the saprophytic phase of soil-borne fungal pathogens in the presence of many heavy metals such as Al, B, Co, Li, Mn, Mo and Zn together with a statistical interpretation of the triple interaction: micro-elements, concentrations and incubation periods was indicated by Sulochana (1952 a-d).

The symptomatology of Fusariose wilt of cotton has been studied in detail particularly in relation to internal changes such as ascorbic acid, chlorophyll and reducing sugar contents; histological changes in the diseased vein-cleared leaves were mainly elongation and shrivelling of the palisade cells and a reduction in the number of chloroplastids. During the progress of the disease, starch synthesis was inhibited during light periods, but normal translocation continued during dark periods indicating no serious derangement of phloem function (Kalyanasundaram, 1954b). Similarly, work on non-protein and protein nitrogen (NPN and PN respectively) indicated that the result of pathogenesis appeared to be a decrease in the available NPN constituents of the host which is suggestive of the operation of the enzyme systems of *Fusarium vasinfectum* (Sadasivan and Subramanian, 1954a; Lakshminarayanan, 1955a). External vein-clearing symptoms with onset of disease was completely described for the first time (Satyanarayana and Kalyanasundaram, 1952). The screening of toxin-invaded plants under ultra-violet illumination was described by Subba Rao (1954).

Much evidence has been presented by many workers in this laboratory in the elucidation of the mechanism of Fusariose wilts (Sadasivan, 1955; Kalyanasundaram, 1955b; Lakshminarayanan, 1955a; Subramanian, 1955c). The highlights of these investigations may briefly be summarised as follows: There is overwhelming evidence to show that the disease syndrome is the result of toxaemia rather than one solely of mechanical vessel plugging induced by pectic enzymes or polysaccharides, etc. The demonstration of the production of Fusaric acid *in vivo* in cotton plants infected by the fungus was made by using an elegant chromatographic technique, chelating the Fusaric acid from internal tissues of the host with copper which gave specific R_f values (Lakshminarayanan and Subramanian, 1955). This has been confirmed further by using a bioassay cum chromatographic technique (Kalyanasundaram and Venkataram, 1956). It has also been shown that *Fusarium vasinfectum* produces antibiotics in the unsterilized soil which is a finding of considerable significance (Kalyanasundaram, 1955c).

Study of enzyme systems both of the cotton plant and *Fusarium vasinfectum* has yielded fruitous results. For instance, sizeable quantities of cysteine along with other major amino acids like asparagine and glutamine were present in the resistant varieties of cotton examined but were absent in a susceptible cotton variety tested and it is suggestive of this cysteine of the resistant variety of cotton chelating with Fe''' available in the host and rendering this quantum of iron unavailable for chelation with the toxin which appears to be a pre-requisite for toxigenic wilting of cotton (Lakshminarayanan, 1955b). Pre-treatment with an optimum concentration of 5-10 ppm. of 8-quinolinol was found to give effective protection to cut shoots of cotton against toxaemia to dialysed culture filtrates of *Fusarium vasinfectum.* The chemotherapeutant was also effective *in vivo* in sand cultures (D. Subramanian, 1956). Further work on pectin methyl esterase and pectin galacturonase activity of Fusaria indicated that high root pectin content of cotton plants seems to be correlated with susceptibility and low levels with resistance and the main seat of pectin synthesis and storage in the susceptible variety is the root while it is the shoots and leaves that accumulate higher pectic reserves in the resistant cotton varieties studied. Therefore, the pathogen despite its ability to utilize pectin substrates is denied such a source from the roots of resistant varieties thereby rendering its pectic enzyme systems inoperative (Lakshminarayanan, 1956b). It is relevant to mention here that the emphasis in studying amino acid build-up in

plants has now shifted to one of examining root exudates as exosmosis of these pectin fractions has come to be regarded as not only in the realm of theoretical possibility but one of practical importance and, indeed, does take place. Recent work in this field in this laboratory has thrown considerable light and indicates differences in the amino acid exudates from resistant and susceptible rice plants to the foot rot fungus, *Fusarium moniliforme* (Andal, Bhuvaneswari and Subba Rao, 1956; Andal and Subba Rao, 1956).

Growth factor studies have been carried out with many genera of tropical fungi such as *Pellicularia koleroga, Piricularia* spp., *Sclerotium oryzae, Corticium microsclerotia* and *Cercospora personata* (Mathew, 1952, 1953, 1954b; Sadasivan and Subramanian, 1954b; Apparao, Saraswathi-Devi and Suryanarayanan, 1954). Eleven isolates of *Pellicularia koleroga* were found to be heterotrophic to thiamine, but their capacity to synthesise this vitamin was not completely lost as they do well in a mixture of thiazole and pyrimidine or pyrimidine alone. *Piricularia oryzae*, however, was unable to do this in young cultures, but with advancing age utilizes an equimolar mixture of thiazole and pyrimidine or pyrimidine alone. Further work on growth requirements of *Piricularia oryzae* showed that thiamine, and iron and zinc, and possibly copper, are indispensable for growth but, nevertheless, interdependent in their action.

Work on other aspects of the physiology of fungi can be summarised as follows: the physiology of Fusaria has been studied in detail. Aeration stimulated mycelial growth but inhibited sporulation although it had no effect on pH of the medium (Sarojini and Yogeswari, 1947). Carbon, nitrogen and pH relationships to the growth of Fusaria showed that there were differences between species in so far as growth, their sugar and nitrogen utilization and shifts in the pH of the media are concerned (Srinivasa Pai, 1953). Sporulation varied with the source of nitrogen, urea being the best, followed by potassium nitrate and ammonium sources (Subramanian and Srinivasa Pai, 1953). Similar studies on *Piricularia oryzae* showed that the fungus failed to utilize the usual inorganic ammonium nitrogen sources such as ammonium chloride, ammonium sulphate and ammonium nitrate, whereas it readily utilised other nitrate sources. Organic acids such as fumaric, succinic, tartaric, citric, oxalic, acetic and lactic acids, or addition of calcium carbonate stimulated growth and aided utilization of inorganic ammonia. It was thus clear that utilization of different forms of

nitrogen would depend on pH changes and in this process organic acids or calcium carbonate act as buffering agents and help in the maintenance of pH at an optimum level.

More recent work has indicated the essentiality of certain heavy metals to growth and sporulation of Fusaria using bioassay techniques (using *Aspergillus niger*, 'M' and 'M.U.B.L.1' strains). Work on different strains of *A. niger* has shown different degrees of sensitivity in the detection of heavy metals (Saraswathi-Devi, 1954a, 1955). The Madras strain (M.U.B.L.1) was found to be less sensitive to traces of manganese and more sensitive to copper, and perhaps molybdenum also, than the standard Mulder strain ('M' strain). Quite recently, spectrochemical studies have been initiated in studying uptake of metabolites by wilted plants and the consequent derangement thereof in the mobility of ions. It has been shown, using the standard Lundegårdh (spark-in-flame) technique that cotton plants infected by *Fusarium vasinfectum* showed an increased uptake of magnesium, calcium, iron and manganese and decreased accumulation of potassium over the healthy controls. It has been suggested that the derangement in the selective absorption of ions, seen in the infected plants, is more likely to have been caused by chemical agents (toxins) than physical causes such as plugging of vessels (Sadasivan and Kalyanasundaram, 1956). Confirmation of this was obtained from studies on the conductivity of roots, stems and leaves of infected cotton plants which showed a remarkable fluctuation in the ionic concentration of the tissues prior to the appearance of systemic symptoms; with the appearance of symptoms in the leaves, the conductivity of the tissues showed an increase over the healthy, indicating accumulation of electrolytes (Gnanam, 1956).

In the field of systematic mycology, detailed studies were made on the fungus floras of soils and the rhizosphere of crop plants. Soil Fusaria and Fusaria infecting crop plants were intensively investigated and systematic accounts have been published (Subramanian, 1951a, 1952a, 1952d, 1954b; Prasanna Varma, 1954; Venkataram, 1955b). The question of the "wild type" in the genus *Fusarium* has been considered in the light of work on a large number of fresh isolates of different species obtained from soils as well as from crop plants; it was concluded that species of *Fusarium* occur in nature in a multiplicity of forms and not as a single "wild type" (Subramanian, 1951b, 1955b). More recently, problems re-

lating to classification of Fusaria were also critically reviewed and discussed (Subramanian, 1955a).

Apart from studies on soil fungi, considerable work has also been carried out on other saprophytic and parasitic fungi which include many new records for India and many new taxa. The Fungi Imperfecti have received much attention and twenty-two new genera have been described, of which sixteen are hyphomycetes and six are coelomycetes. The new hyphomycete genera described are *Beltraniella* Subramanian (1952c), *Lacellinopsis* Subramanian (1953a), *Koorchaloma* Subramanian (1953c), *Lomaantha* Subramanian (1954a), *Lomachashaka* Subramanian (1956a), *Paathramaya* Subramanian (1956a), *Prathoda* Subramanian (1956a), *Tharoopama* Subramanian (1956a), *Phaeotrichoconis* Subramanian (1956c), *Prathigada* Subramanian (Subramanian and Ramakrishnan, 1956d), *Dwayamala* Subramanian (1956e), *Kutilakesa* Subramanian (1956e), *Nalanthamala* Subramanian (1956e), *Bahusandhika* Subramanian (1956e), *Vakrabeeja* Subramanian (1956e) and *Starkeyomyces* Agnihothrudu (1956b); the six new coelomycete genera are *Plagionema* Subramanian & Ramakrishnan (1953c), *Rostrospora* Subramanian & Ramakrishnan (1952), *Petrakomyces* Subramanian & Ramakrishnan (1953a), *Anthasthoopa* Subramanian & Ramakrishnan (1956a), *Alpakesa* Subramanian & Ramakrishnan (1954) and *Shanoria* Subramanian & Ramakrishnan (1956e). In the ascomycetes one new genus of the Hemisphaeriales, *Sapucchaka* Ramakrishnan (1956a) was described. It will be noticed that we have made a departure in naming new genera: most of the names have been derived from our classical language, Sanskrit and not from Greek or Latin. We commend this to workers in countries familiar with this language, particularly because Greek and Latin root sources have been drawn upon rather intensively in the past. Taxonomic studies on hyphomycetes (Subramanian, 1956a, b, c, d, e), and on some genera of the Sphaeropsidales such as *Neottiospora* (Subramanian and Ramakrishnan, 1953b, 1954, 1956b), *Amphichaeta* (Subramanian and Ramakrishnan, 1956c) and *Ciliochorella* (Subramanian and Ramakrishnan, 1956e) have also been in progress. Systematic accounts of Indian species of *Curvularia* (Subramanian, 1953b), and *Periconia* (Subramanian, 1955d) and South Indian myxomycetes (Agnihothrudu, 1954a,b, 1955, 1956a) were published.

A mycological herbarium was started in 1951 and many of the observations and records made from periodical collections of fungi

largely by Drs. Subramanian and Ramakrishnan have yet to be published.

Besides the original publications cited already, two lengthy and important compilations on Indian fungi were also brought out during the period. One is a list of fungi recorded in India during 1938-1952, intended as a successor to Mundkur's *Fungi of India—Supplement I* published in 1938 (Ramakrishnan and Subramanian, 1952). The second, is a similar list covering the period 1952-56 (Subramanian and Ramakrishnan, 1956d). A list of Indian soil fungi, including the larger fungi, was also published in 1952 (Subramanian, 1952f). These lists are largely intended as an aid to workers in systematic mycology and taxonomy of fungi in this country and indeed, contain a very complete bibliography of Indian systematic mycology during the period 1938-1956.

In concluding this brief résumé we feel it our duty to thank several institutions in India, particularly the Indian Academy of Sciences, the National Institute of Sciences, the Current Science Association and the Indian Botanical Society, for much encouragement by publishing our research papers. We also wish to record our deep appreciation of the generous grants-in-aid which have flowed from the Ministry of Education, Government of India and the University Grants Commission and have enabled us to put into operation many precision instruments so vital for modern research methodology in the study of botanical problems.

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LIST OF THESES

MASTER OF SCIENCE

Venkatanathan, T. N. 1932. Studies on *Isoetes coromandelina* L.

Madhusudana Rao, I. 1933. Studies in absorption and transpiration.

Rama Rao Panje. 1933. Contribution to our knowledge of *Balanophora.*

Anavema Reddy, C. K. 1936. Origin and development of root-suckers in *Ixora acuminata* Roxb.

Ganesan, D. 1956. 1. A contribution to the life-history of *Pedalium murex* Linn.
2. Cytological studies in a chromosome ring-forming diploid *Notonia grandiflora* D.L.
3. On the split appearance of chromosomes photographed with infra red rays.

Janet, Mercia. 1936. 1. An investigation of the soil algae of Madras.
2. *Westiellopsis prolifera* sp. et gen. nov., a new member of the Stigonemataceae.
3. The seasonal succession and ecology of the phytoplanktons of an artificial pond in Madras.
4. Daily vertical circulation of water and vertical migration of the plankton algae in an artificial pond in Madras.

John, Rachel P. 1936. The seasonal succession and algal ecology of a permanent pool in Madras.

Ramanathan, K. R. 1936. On the morphology, cytology and alternation of generations in *Enteromorpha compressa* (L.) Grev. var. *lingulata* (J. Ag.) Mauck. On a form of *Anabaenopsis* from Madras.

Srinivasan, K. S. 1937. 1. On the morphology, life-history and cytology of *Riccia himalayensis* St.
2. On an ascomycetous fungus attacking *R. himalayensis.*
3. On the morphology and cytology of *Marchantia palmata.*

Veeraraghavan, K. G. 1937. 1. A four years' study of the phytoplankton of an irrigational tank in South India with special reference to their seasonal succession and periodicity.
2. South Indian species of *Oedogonium* Link.

Venkataraman, G. 1938. Ecology and seasonal succession of the algal flora of the river Cooum at Madras with special reference to Diatomaceae and a systematic account of some South Indian diatoms.

Doraiswami, S. 1940. 1. Nuclear division and cross-wall formation in *Spirogyra.*
2. On the morphology and cytology of *Eudorina indica* Iyengar.

Kanthamma, S. 1940. An investigation of the soil algae of Madras.

Krishna Rao, D. B. 1940. 1. Structure and development of *Hormophysa triquetra* Kutz.
2. On the structure and development of *Turbinaria conoides* Kutz.

Philipose, M. T. 1940. 1. The ecology and seasonal succession of algae in a permanent pool at Madras.
2. *Gleotilopsis,* a new member of the Ulotrichaceae.
3. *Pseudulvella americana* (Snow) Wille growing in Madras.

Vimala Bai, B. 1940. 1. Somatic mitosis and cross-wall formation in some desmids.
2. The germination of zygote in *Cosmarium indicum* sp. nov.
3. A systematic account of some desmids from Kodaikanal lake.

Balakrishnan, M. S. 1941. Contributions to the developmental morphology and cytology of some South Indian Rhodophyceae.

Subrahmanyan, R. 1942. Studies on the life-history and cytology of some South Indian diatoms.

Desikachary, T. V. 1944. Studies on some South Indian Cyanophyceae.

Sundaralingam, V. S. 1944. Contributions on the studies on Indian Characeae.

Saraswathi, M. R. 1944. Contributions to the cytology, developmental morphology and life-history of desmids.

Yogeswari, L. 1947. Nutritional physiology of certain wilt (root-infecting) fungi of plants.

Venkataram, C. S. 1949. Study on cotton seed (1) with special reference to loss of seed viability due to fungal action. (2) Action of fungicides on longevity of cotton seed.

Ponnaiya, B. W. X. 1949. Studies in the genus *Sorghum*.

Sulochana, C. B. 1950. Soil conditions and wilt diseases in plants with special reference to colonization and survival of soil Fusaria in soils treated with micro-elements.

Srinivasa Pai, K. V. 1951. Nitrogen metabolism of soil fungi.

Muthukrishnan, R. 1952. Saprophytic activity of Fusaria in wilt-sick soils.

Shanta, P. 1953. Trace element nutrition of soil fungi with special reference to *Fusarium moniliforme*.

DOCTOR OF PHILOSOPHY

Subramanian, C. V. 1947. Soil conditions and wilt diseases in plants with special reference to *Fusarium vasinfectum* on cotton.

Sarojini, T. S. 1949. Soil conditions and root diseases with special reference to *Fusarium udum* on red gram.

Venkataramani, K. S. 1949. Studies on Indian vegetables.

Thankam, C. 1949. Antagonism between fungi and other micro-organisms in the soil with special reference to *Fusarium* species.

Zachariah, A. T. 1949. Micro-ecology of soils of cultivated fields of South India with special reference to the occurrence and physiology of Fusaria.

Desikachary, T. V. 1950. Contributions to our knowledge of South Indian Algae—Myxophyceae.

Yogeswari, L. 1950. Trace element nutrition of fungi with special reference to *Fusarium* spp.

Chinnayya, E. J. 1951. Soil conditions and wilt diseases in plants with special reference to *Rhizoctonia* spp. on cotton.

Mathew, K. T. 1952. Studies on the black-rot of coffee.

Prasanna Varma, R. 1952. Soil conditions and wilt diseases in plants with special reference to *Fusarium* spp. on tomato.

Radha, K. 1952. Soil conditions and wilt diseases in plants with special reference to *Rhizoctonia bataticola*.

Kalyanasundaram, R. 1953. Soil conditions and wilt diseases in plants: Fungal wilts and changes in host metabolism.

Ramakrishnan, K. 1953. Soil conditions and fungal wilts in plants — The distribution and behaviour of fungi in soil.

Varadarajan, P. D. 1953. Soil conditions and wilt of plants with special reference to trace element nutrition.

Agnihothrudu, V. 1954. Soil conditions and wilt diseases in plants: Rhizosphere microflora in relation to fungal wilts.

Venkataram, C. S. 1954. Fusaria of Southern Indian soils.

Satyanarayana, G. 1955. Soil conditions and wilt of cotton with special reference to host physiology.

Lakshminarayanan, K. 1955. Studies on fungal enzymes, with special reference to the *Fusarium* wilt of cotton.

Suryanarayanan, S. 1955. Growth factor requirements of some fungi.

THESES SUBMITTED

Saraswathi-Devi, L. 1956. Soil conditions and wilt diseases in plants: Essentiality of trace elements to some soil fungi.

Appa Rao, A. 1956. Studies on the blast disease of rice.

Lakshmanan, M. 1956. Host-parasite relationship in plant wilts with special reference to respiration.

Subramanian, D. 1956. Studies on the control of fungal wilts of plants.

Department of Biochemistry

The research work carried out in this department can be broadly divided into two sections, one dealing with investigations carried out between the years 1933 and 1948 when Dr. M. Damodaran developed a school of biochemical research with emphasis on studies of proteins, peptides and proteolytic enzymes and the second between the years 1949 and 1956 when Dr. P. S. Sarma developed a school of research with emphasis on water soluble vitamins and their inter-relationships and on biochemical investigations using radioactive isotopes.

Damodaran and Sivaswamy (1936) isolated 'anacardein' from cashew nut (*Anacardium occidentale*), in yields amounting to 18 per cent of the fat free seed. In analysing this protein according to the Van Slyke nitrogen distribution method, it was found that the precipitate obtained with phosphotungstic acid was completely free from sulphur, even though the presence of cystine in the protein has been established beyond doubt. Further studies showed that the extent of precipitation at any particular temperature is dependent on the concentration of cystine content and that below a certain minimum concentration of cystine, there was no precipitation. Hence, certain proteins may contain cystine and still show no cystine sulphur in the phosphotungstic acid precipitate.

Krishnan and Krishnaswamy (1939) investigated the proteins and other nitrogenous constituents of water melon seeds (*Citrullus vulgaris*) and isolated one globulin in a crystalline condition. Damodaran and Narayanan in the same year studied the seeds of *Canavalia obtusifolia,* and showed that they had high urease activity and that they were a good source of the amino acid 'canavanine'.

Damodaran and Ramachandran (1940, 1941) have isolated a trypsin resistant phosphopeptone of constant composition in the form of its barium salt by digesting 'para-nuclein' which separated as an insoluble complex when casein was digested with pepsin. From their results of analysis, the authors have concluded that the phosphopeptone is a polypeptide of ten amino acids made up of three molecules each of glutamic acid and isoleucine and four molecules of serine.

In the field of enzymes, Damodaran and Sivaramakrishnan (1937) showed that the seeds of the water melon (*Citrullus vulgaris*) were a potent source of urease, and that this urease preparation was better than those obtained from soya bean or jack bean for urea determinations. Later, Damodaran and Sivaramakrishnan (1946) have shown that for the estimation of urea in biological fluids, the water melon urease was far more satisfactory than the usual urease preparations from soya bean or jack bean.

Srinivasan (1936) obtained an enzyme preparation from the pressed juice of drumstick (*Moringa pterygosperma*). This enzyme which oxidised ascorbic acid and hence called ascorbic acid oxidase was studied in detail in regard to its properties and also the kinetics of enzymic reaction.

Damodaran and co-workers have also carried out studies on some of the basic problems of enzymic proteolysis. Thus a systematic study has been conducted on ammonia formation and on hydrolysis of peptide linkages during the action of pepsin, trypsin, erepsin and papain. Three typical proteins,casein, edestin and gliadin were used. It was found that the amide and peptide hydrolysis do not run parallel and that the ammonia formed was mainly due to the decomposition of the primary products of protein hydrolysis. The secondary decomposition was not due to enzymic action, but was the result of acidic or alkaline reaction of the digestion mixture. In a subsequent experiment, Damodaran and Narayanan (1938) have studied the action of these enzymes on various amides, and have established the specificity of the proteolytic enzymes in relation to the 'amide' nitrogen of proteins. Further, there has been considerable difference of opinion as to the formation of free amino acids, particularly tyrosine during the digestion of proteins by pepsin. It was generally held that pepsin splits proteins into higher peptides from which amino acids were liberated only by the further action of other specific enzymes called peptidases. Damodaran and Krishnan (1938) have obtained clear evidence to show that tyrosine was liberated during peptic digestion of casein.

The properties of glutamic acid dehydrogenase from germinating seeds have been investigated by Damodaran and Ramakrishnan Nair (1938). It was found that the enzyme was present in the seedlings of *Phaseolus mungo*, and the purified enzyme was found to oxidise naturally occurring l-glutamic acid thus differing from deaminase of animal origin. The properties of the purified enzyme have also been studied.

Damodaran and Ramaswamy (1940) have investigated the succinic dehydrogenase activity in germinating seeds with a view to study the mechanism of formation of asparagine. It was observed that all leguminosae seeds tested showed succinic dehydrogenase activity on germination. This enzyme was, however, absent in seedlings of the water melon and of rice. The authors have suggested that in the leguminoseae, the accumulation of asparagine during germination took place at the expense of glutamic acid, succinic acid being formed from the latter. The aspargine was then formed from succinic acid and ammonia.

A comparative study of the enzymes arginase and canavanase from both animal and plant sources has been made by Damodaran and Ananthanarayanan (1940). Their findings have indicated a close parallelism between the activities of arginase and canavanase. The behaviour of the two enzymes on autolysis and in presence of cobalt ions indicated that the two enzymes may be identical.

Yeshoda (1941) worked out a method for obtaining the milk clotting enzyme of *Withania coagulans* in a highly concentrated form. This enzyme had no proteolytic activity, a point of interest throwing light on the mechanism of clot formation, which was considered by some to involve a proteolytic breakdown of the casein prior to coagulation.

Damodaran and Subramanian (1948) have investigated the amino acid changes and also urea formation during germination of seeds. The presence of the enzyme 'aspartase' which converts aspartic acid to fumaric acid and ammonia has been demonstrated in seedlings of *Phaseolus mungo, Cicer arietinum,* and *P. sativum.*

Studies on Ascorbic Acid :

Using uniformly C^{14} labelled radioactive glucose, the direct conversion of glucose to ascorbic acid has been shown to take place in germinated seedlings. The influence of ammonium sulphate on the biosynthesis of ascorbic acid has also been studied by Sivarama Sastry and Sarma (1956). Further, the percentage conversions of radioactive glucose, fructose and sucrose to radioactive ascorbic acid in germinating green gram seeds were determined. It was found that all the three sugars were converted to ascorbic acid to the same extent. The influence of vitamins of the 'B' group on the biosynthesis of ascorbic acid has been investigated by employing the corresponding anti-vitamins and it has been shown that thiamine, pyridoxine and pantothenic acid play a significant role

in the various enzymic steps involved in this conversion (Thangamani and Sarma, 1956).

Studies on nicotinic acid and its inter-relationship with tryptophane:

The factors which affect the conversion of tryptophane to nicotinic acid in various systems as in *Neurospora crassa,* germinating seeds, rice moth larvae (*Corcyra cephalonica* st.), and the albino rat have been studied particularly from the point of view of the influence of (i) various 'B' vitamins, (ii) proteins and amino acids and (iii) various carbohydrates. Using anti-vitamins, it has been shown that pyridoxine, folic acid and biotin are involved in the biological synthesis of nicotinic acid from tryptophane (Shanmugasundaram and Sarma, 1953). As regards proteins and amino acids, it has been found that protein hydrolysate and certain amino acids inhibit the utilization of tryptophane, kynurenine and 3-hydroxy kynurenine but that they do not have any action on the utilization of 3-hydroxy anthranilic acid and nicotinic acid. It was also found that in the case of germinating seeds the presence of fructose lowers the biosynthesis of nicotinic acid whereas glucose had no such effect.

The metabolism of nicotinic acid and nicotinamide studied in the rice moth larvae has shown that it differed in certain important respects from that observed in higher animals. Thus, neither form of this vitamin is methylated prior to excretion and the main excretory metabolite is free nicotinic acid, irrespective of whether nicotinic acid or nicotinamide is given in the larval diet. Nicotinuric acid, the glycine conjugate of nicotinic acid has also been found to be excreted in significant amounts (Sundaram and Sarma, 1956). A system bringing about deamidation of nicotinamide has been investigated in the rice moth larvae and in *Neurospora crassa* and its locale in the cellular organisation of the organism was found to be the soluble cytoplasmic material.

Studies on Biotin and Inositol:

A deficiency of biotin was found to produce in the rat, a higher retention of nitrogen. The urea excretion and the per cent of ingested nitrogen converted into and excreted as urea, as also the ratio of urea nitrogen to urinary nitrogen were all found to decrease appreciably, when the animals developed an uncompli-

cated deficiency of this vitamin (Siva Sankar and Sarma, 1952). A similar accumulation of nitrogen was also found in the tissues of biotin deficient larvae. Ramachandran and Sarma (1955) have found that the gamma isomer of hexachlorocyclohexane the anti-vitamin of inositol inhibited the synthesis and secretion of amylase in pigeon pancreatic slices in the same manner as a dietary deficiency of inositol. Further, biotin was found to reverse the effect of the gamma isomer on amylase formation by obviously stimulating the synthesis of inositol.

Paper chromotagraphic Separation of 'B' group of Vitamins :

The separation and identification of all the members of the vitamin 'B' complex excepting folic acid have been achieved by ascending paper chromatography using a new solvent system consisting of n-butanol, methanol, benzene and water. Folic acid was detected as well as estimated by the same technique employing phenol saturated with water as the solvent system (Radhakrishnamurthy and Sarma, 1953). Further, a useful modification in the technique of ascending paper chromatography was devised to facilitate better separation of constituents which have close and low R_f values, by employing a pad of filter paper discs to provide extra capillary absorption.

Studies on Shark Liver residue as a rich source of 'B' vitamins :

Shark liver residue left over as waste material after extraction of liver oil was investigated for its possible utilization as a cheap source of nutritionally essential factors (Rajagopalan and Sarma, 1956). Proteolysed extracts prepared from liver residues were analyzed for the following 'B' vitamins, thiamine, riboflavin, nicotinic acid, pantothenic acid, vitamin B_6, folic acid, vitamin B_{12}, biotin, choline and inositol. It was found that the liver residue could be used as a very good source for the preparation of liver extracts of appreciable nutritional potency.

The Influence of 'B' Vitamins on nitrogen metabolism :

The role of 'B' vitamins, thiamine, biotin, p-amino benzoic acid, folic acid and pantothenic acid in amino acid metabolism in germinating green gram seeds (*Phaseolus radiatus*) has been investigated. It was found that during germination, there was a rapid fall in glutamic acid and a marked increase in the level of aspartic acid. Both the anti-vitamins of thiamine and biotin produced an

accumulation of glutamic acid and a corresponding fall in aspartic acid. Sulphanilamide produced an accumulation of histidine and arginine and a fall in the level of methionine and serine. Using glutamic acid and glucose, both uniformly labelled with C^{14}, the biosynthesis of asparagine has been studied in three species of legume seeds and using C^{14} labelled glucose, evidence has been obtained for the rapid synthesis of glutamic acid during germination (Sivaramakrishnan and Sarma, 1955)

Studies on the nutritive value of reconstituted milk:

Reconstituted milk, as prepared by the Government Milk Factory, Teynampet, Madras, has been found to be inferior in nutritive value, to fresh cow's milk or to toned milk as shown by growth experiments with albino rats. Estimation of different vitamins by chemical, spectrophotometric and microbiological methods showed that reconstituted milk had a lower vitamin value in regard to most of the vitamins investigated than eiher cow's milk or toned milk.

The growth promoting value of reconstituted milk for rats was not improved by supplements of different amino acids and vitamins but was improved markedly on supplementation with casein showing that the lower growth promoting value of reconstituted milk was probably due to its low strepogenin content. Also evidence was obtained for the presence in skim milk powder stored at 37°C and 60°C of a substance toxic to *Lactobacillus bulgaricus* 09 This growth inhibitor was obtained in a concentrated form and its properties studied. The data obtained suggest that it is peptide in nature and possessed anti-strepogenin activity.

Studies on phosphatases and phosphoproteins :

Highly active preparations of French bean pyrophosphatase were obtained by the following methods (i) fractional precipitation with acetone, (ii) fractional precipitation with ammonium sulphate and (iii) adsorption on calcium phosphate gel and subsequent elution with five per cent sodium chloride and finally dialysis. The product thus obtained was about hundred times as active as the crude extracts of the seeds. The purified pyrophosphatase did not show any activity towards sodium β-glycerophosphate, but it liberated orthophosphate phosphorus from sodium pyrophosphate, adenosine triphosphate and thiamine pyrophosphate. The optimum pH and the effect of various inhibitors and activators have been studied.

A phosphatase specific for the dephosphorylation of phosphoproteins was detected in the tissues of higher animals and in oil seeds (Sundararajan and Sarma, 1953). The purification and characterization of this relatively little known enzyme has been studied in detail. An enzymic method for the preparation of dephosphorised casein has also been developed as a result of these studies. Amino acid analysis and other studies carried out on the dephosphorylated protein have shown the superiority of the enzymic method over the existing chemical methods. Further, an investigation of the biosynthesis of casein in the lactating mammary gland of rat has been carried out and evidence has been obtained to indicate the presence in this tissue of an active enzyme needed for the phosphorylation of proteins.

Studies on the Biochemical role of Zinc :

The growth inhibition produced by excess dietary zinc in rice moth larvae was found to be counteracted by whole liver extract, the alkali stable fraction of liver extract and by desoxy ribonucleic acid. None of the 'B' vitamins was effective in this respect with the possible exception of vitamin B_{12}. The inhibition in catalase levels observed in zinc toxicosis was reversed by copper.

Cystine caused a specific growth inhibition and fat accumulation in rice moth larvae which was reversed by tryptophane and to a lesser extent by nicotinic acid. Zinc sulphate at physiological levels was partially effective in this condition.

In cholesterol fed rats, the *in vitro* uptake of radioactive zinc (Zn^{65}) by erythrocytes decreased, these values being very nearly normal when zinc was also added to the diet. The distribution of radioactive zinc in the livers of rats also followed the same pattern.

Biochemical studies on thyroid hormone :

The optimum conditions for maximum thyroxine formation on iodination of different proteins have been studied. Shark ray collagen, a scleroprotein has been shown to yield a high percentage of thyroxine when compared with other scleroproteins like silk fibroin. In the field of protein iodine interaction, it was observed that the hydroxy-amino acids (threonine, serine, and hydroxyproline) in the free as well as in the bound form in proteins, were completely oxidized by iodine. Further, cysteic acid, the oxidation product of cystine was shown to be formed on iodinating proteins. A new colorimetric method of determining diiodotyrosine has been

developed using the metal chelating property of diiodotyrosine (Moudgal, Ramachandran and Sarma, 1954).

Investigations carried out on the goitregenic action of groundnut in albino rats have shown that the goitregenic factor is an anthocyanin, arachidoside, present in the red pigment of seed coats. This goitregenic action is overcome by additions of small amounts of iodine to the diet. Tracer technique involving the use of radioactive iodine (I^{131}) has conclusively proved that arachidoside is the goitregenic factor. On similar lines, an anthocyanin isolated from cashew nut red seed coat has been found to be goitregenic. Tracer studies with radioactive iodine have further shown that mode of action of these goitregenic agents consists in competing with tyrosine for elemental iodine in the thyroid tissue.

During the course of investigation on the metabolic role of thyroid hormone in the animal body the following interesting observations have been made. Thyroid hormone was found to influence biological methylation systems in the animal body. Thyroid imbalance was also found to affect glucuronide conjugation in the rat. Further, *in vivo* as well as *in vitro* experiments have shown that thyroxine can depress the activity of enzyme catalase. Feeding iodoamino acids to rice moth larvae was found to affect growth, metamorphosis and oxygen consumption (Srinivasan, Moudgal and Sarma, 1955).

Studies on the preservation of Neera :

Among the various substances tried for the preservation of 'Neera' the sweet palm juice, the anti-malarial substance 'Paludrine' has been found to be quite effective in keeping Neera in an unfermented state for a period of fifty four hours. The maximum concentration of 'Paludrine' needed was one in five thousand parts though generally, lower concentrations were found to be sufficient if weather conditions were favourable. Extensive field trials conducted at Udangudi in Tinnevelly District have shown that Neera preserved with 'Paludrine' gave higher yields of palm gur and sugar. Further, the gur prepared without 'Paludrine' got contaminated with various fungi and its keeping quality was very poor whereas the gur prepared from Neera preserved with 'Paludrine' was free from any contamination or mouldy growth on the surface. A patent has been obtained for this process by the Council of Scientific and Industrial Research. It may be stated that feeding trials with albino rats for over hundred days have shown that

daily addition to the diet of 'Paludrine' at a concentration of thirty milligrams per cent did not produce any untoward symptoms or affect the rate of growth of young albino rats.

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APPENDIX I

List of Research Students who were Awarded Research Degrees in Biochemistry, University of Madras

M.Sc. DEGREE

Sivaswamy, T. G. 1937. A New Globulin from Cashew Nut.

Devi, Miss P. 1937. Chemical Composition of the Fat from the Seeds of *Carcinia indica*.

Krishnan, P. S. 1938. The Globulin from the Seeds of Water Melon.

Krishnaswamy, T. K. 1938. A New Glutelin from the Seeds of Water Melon.

Ramaswamy, R. 1938 Isolation of 1′-3-4 Dehydroxy-phenylalanine from the Seeds of *Mucuna pruriens*.

Anantanarayanan, K. G. 1939. Isolation of Canavanine from the Seeds of *Canavalia obtusifolia*.

Narayanan, E. K. 1939. On the Specificity of Proteolytic Enzymes-amide Hydrolysis.

Sivaramakrishnan, P. M. 1939. Water Melon Urease.

Ramakrishnan Nair, K. 1940. (i) Glutamic Dehydrogenases from Germinating Seeds (ii) A tannin from Indian Gooseberry with a Protective Action on Ascorbic Acid.

Ramachandran, B. V. 1940. Amino Acids of Casein Phosphopeptone.

Venkatesan, T. R. 1941 Amino Acid Changes in Germinating Seeds.

Srinivasan, V. R. 1943. Nitrate Reduction in Plants.

Vijayaragavan, P. K. 1945. Biological Value of Proteins with Special Reference to Blood Regeneration.

Roberts, G. W. 1946. Blood Regeneration in Phenylhydrazine Anaemia with Special Reference to Changes that Take Place in the Bone Marrow and Blood and Iron Metabolism.

Kerala Varma, 1947. Mechanism of Symbiotic Nitrogen Fixation by Leguminosae.

Rangachari, P. N. 1947. Pectin Content of Indian Plant Materials with an Investigation on Tamarind Seed Mucilage.

Subramaniyam, S. 1948. Bacterial Oxidation of Sorbitol to Sorbose.

Ninan, Verghese, 1948. Kidney Proteins.

Visvanathan, R. 1949. Enzymic Hydrolysis of Starch.

Chandran, K. 1949. Isoleucine in Nutrition with Special Reference to Haemopoiesis.

Siva Sankar, D. V. 1949. Proteins and Other Nitrogenous Constituents of the Castor Seed.

Lakshminarayanan, K. 1950. Microbial Enzymes.

Friedmann, H. C. 1950. Enzyme Studies on Hepatic Adenosine Triphosphate Breakdown.

Ramachandran, L. K. 1951. Studies on the Hydroxyamino Acids, Hydroxylysine, Serine, and Threonine.

Sundararajan, T. A. 1952. Phosphoproteins.

Tirunarayanan, M. O. 1953. Studies on Biotin.

Ranganathan, G. 1953. Carbohydrate Metabolism: Studies on the Biosynthesis of Ascorbic Acid.

Ramachandran, S. 1954. Investigation on the Enzymic Role of Biotin and Inositol.

Rajagopalan, K. V. 1954. Investigations on Shark and other Fish Liver Residues.

Moudgal, N. R. 1954. Biochemistry of Iodoproteins.

Sivarama Sastry, K. 1955. Studies on Ascorbic Acid.

Ph. D. Degree

Narayanaswamy, A. 1948. Protein Structure-Studies on Shark Ray Collagen.

Ramachandran, M. 1950. Tryptophane in Proteins.

Siva Sankar, D. V. 1951. Unsaturated Fatty Acids and Their Vitamin Interrelationship.

Ramachandran, L. K. 1953. Some Studies on Protein, Protein Constituents and Other Iodinated Derivatives.

Shanmugasundaram, E. R. B. 1953. Inter-relationship among some Vitamins and Amino Acids.

Sivaramakrishnan, V. M. 1955. The Influence of Certain Vitamins on Nitrogen Metabolism.

Srinivasan, V. 1955. Biochemical Studies on Iodoproteins and Goitregenic Agents.

Sundaram, T. K. 1955. Influence of Vitamins on Excretory Pigments.

Radhakrishnamurthy, R. 1955. Studies on the Inter-relationship among Vitamins of the 'B' Group.

Sundarajan, T. A. 1955. Studies on the Dephosphorylation of Phosphoproteins.

D.Sc. Degree

Srinivasan, M. 1942. Ascorbic Acid Potency of the Indian Gooseberry (*Phyllanthus emblica*) and the Preparation, Properties, and Application of Ascorbic Acid Oxidase.

Department of Organic Chemistry

The Department of Organic Chemistry has in view the development of research along synthetic approaches to analogues of naturally occurring substances, and the isolation and structure determination of the active principles of vegetable drugs.

On the synthetic side work is in progress on nitrogen heterocyclic compounds. The quinazoline group has many attractive features about it and as a preliminary, the synthesis of a few 4-phenyl quinazolines was effected. This has been followed by the synthesis of 4-benzyl-quinazoline and in view of its close relationship to benzyl isoquinolines, the synthesis of alkyl and alkyloxy substituted 4-benzyl quinazolines is being persued. The synthesis of a number of 3-substituted-2-methyl-4-quinazolones, with halogen and alkyl substituents in the benzene ring has been carried out. The preparation of a few 3 : 4-quinozolonyl quinazolines, which are structurally analogous to the alkaloids Evodiamine and Rutaecarpine, was effected.

In the indole group, a convenient method for the preparation of indole-3-aldehyde has been developed, arising from studies on the mechanism of conversion of gramine to indole-3-aldehyde by reaction with hexamine. The method consists in adding a solution of an equimolecular mixture of indole or substituted indole and hexamine in dilute organic acids to a refluxing solution of another mole of hexamine in the same solvent. Indole-3-aldehyde and 2-phenylindole-3-aldehyde have thus been obtained in 60% and 99% yields respectively. The yields of aldehydes with alkylindoles are much lower and very from 15 to 40%.

Consequent to the finding that skatole participates in the Mannich reaction to give N-dialkylaminomethyl bases, a study has been undertaken to investigate if other 3-substituted indoles also react likewise. 3-Ethyl indole, 3-phenylindole, 2:3-dimethylindole, 2-methyl-3-ethylindole, 3-cyanoindole and also 2:5-dimethyl pyrrole have been found to give N-Mannich bases. 3-Benzylindole, 2-methyl-3-benzylindole and 2-phenyl-3-methylindole, while they do Mannich bases under the same conditions, have, however, afforded neutral products whose structures are under investigation. Most of the derivatives of indole that have been reported so far to give Mannich bases have the 3-position free, which gets substituted

by the entering dialkylaminomethyl group. The orientation is probably on account of the activation of carbon-3 due to the lone pair of electrons on the nitrogen atom of the indole nucleus. Evidently, when position-3 is blocked by a substituent, the dialkyl-aminomethyl group gets linked to the relatively electron-rich N-atom itself. Electron releasing and electron attracting groups in position-3 may be expected to favour or hinder respectively the formation of N-Mannich bases. The yields of Mannich bases obtained with the substituted indoles seem to bear out this expectation.

1-Dimethylaminomethyl skatole and its methiodide were employed as intermediates in the synthesis of 3-methyl-1-isotryptophane. 1-Methylgramine and its methiodide are good alkylating agents. It was of interest, therefore, to study alkylations with the skatole derivatives. Free 1-dimethylaminomethyl skatole displayed a pronounced tendency to reverse to skatole and proved to be a poor alkylating agent. Its methiodide, however, has alkylating properties comparable with those of 1-methyl-gramine methiodide. Sodium cyanide, ethyl malonate, nitroethane and phenyl magnesium bromide all undergo alkylation with 1-dimethylaminomethyl skatole methiodide to give satisfactory yields of N-substituted skatoles. Amine exchange reactions were also carried out, demonstrating parallelism in alkylating properties.

It has been established that a slight alteration in the structure of a compound involved in the chemical process, whereby living cells are produced and maintained, may give rise to a substance which interferes with or inhibits the activity of, the parent compound. Such compounds are of interest as potential antibacterial agents. Among the structural changes which have been effective in such conversions is the introduction of substituents like halogen, alkyl, hydroxyl, etc., or the replacement of one by the other of the isosteric groups –NH–, –O–, –S–, –CH : CH– in the structure of metabolites. Analogues of tryptophane are of interest in view of the important role that amino acid plays in metabolic processes. The synthesis of some analogues of tryptophane has been undertaken. The synthesis of dl-3-methyl-1-isotryptophane was achieved as follows:

Skatole ⟶ 1-Dimethylaminomethyl skatole ⟶ 1-dimethylaminomethyl skatole methiodide ⟶ Ethyl-β (1-skatyl) -α-cyano-α-acetamidopropionate ⟶ 3-methyl–1–iso–tryptophane.

The synthesis of 3-methyl-2-isotryptophane was carried out as follows:

Ethyl benzene ⟶ O-nitro ethyl benzene ⟶ O-amino ethyl benzene ⟶ O-chloracetamido ethyl benzene ⟶ O-dimethylamino acetamodoethyl benzene ⟶ 3-methyl-2-isogramine ⟶ 3-methyl-2-isogramine methiodide ⟶ ethyl-β (2-skatyl)–α -acetamidopropionate → 3-methyl-2-isotryptophane.

Work is in progress to synthesise 1-isotryptophane itself by a series of reactions starting from indole-3-aldehyde. One of the intermediates, ethyl-β (3-cyano-1-indolyl)–α–acetamido–α–cyano-propionate has been prepared.

With a view to preparing analogues of physiologically active compounds which contain the indole nucleus and for whose synthesis indole is employed, methods of synthesis of thiopheno-(2, 3 : 2′, 3′)-pyrrole are being studied.

Work is in progress to utilise tryptophane, which is fairly easily prepared by Mannich reaction, to synthesize members of the β–carboline group and then to take advantage of the presence of the carboxyl group to build up a fourth condensed ring structure. A few members of α-pyridyl-indoles have been synthesized. Closely allied to this is the synthesis of pyrido-pyrimidines. Methyl-2-amino-pyridines, with the exception of the 6-methyl base, reacted homogeneously with β–iodo-propionic acid to afford 3, 4-dihydro-2 H-pyrido-(1, 2a)-pyrimidine–2–ones. In the case of 6–methyl–2–amino–pyridine two products were obtained, the desired pyrimidine-2-one was obtained only in poor yield. There are only very few known representatives of pyrimidine derivatives carrying a heterocyclic ring in position-2. Of the various possible routes for the synthesis of members of this group, the reactivity of malondiamide to ring closure is under examination. The condensation of O-phenylene-diamine with quinoline-2, 3–, 4–, 5–, 6–, 7–, and 8-carboxylic acids have been carried out to obtain 2-quinolyl-benzimidazoles.

In the isoquinoline series a convenient method has been worked out for the synthesis of 1-(2′, 5′-dimethoxybenzyl)-3-methyl-3 : 4-dihydro-6, 7-methylenedioxy isoquinoline. As a corollary to this, all the seven quinoline carboxylic acids have been condensed with α–methyl homopiperonyl amine and the amides cyclised to give 1-quinolyl-3-methyl-3: 4-dihydro-6, 7–methylenedioxy isoquino–lines.

The condensation of lithium α-picoline with epichlorhydrin is being investigated. The reaction proceeds fairly smoothly and a homogeneous product has been obtained. A rigid proof of its constitution is being worked out.

A group of workers are engaged on the addition of thioglycolic acid to double bonds. Methyl thioglycolate very readily adds on to methyl cinnamate under the catalytic influence of piperidine in the absence of a solvent. When the reaction is carried out using dry sodium methoxide in benzene, cyclisation also seems to take place. With benzal azlactone in absolute methanol and a few drops of piperidine, addition, opening of the azlactone ring and esterification take place with facility. These products are preliminary steps in a projected synthesis of 2-phenyl-5-ketoimidazolido-thiophane and 2-keto-4-phenyl-2, 3, 4, 6-tetrahydro-thieno- (3, 4)-imidazole. The addition of thioglycolic acid to Schiff-bases is also under study.

In the homocyclic series, one line of work is the synthesis of naphthaquinones with alkyl and alkyl-oxy substituents in the non-quinonoid nucleus. The interest in this group of compounds stems from the chemistry of Sea Urchin colouring matter, which is of great physiological and biochemical interest. Before entering into the synthesis of polysubstituted quinones, a start has been made with the synthesis of 6-methyl-7-methoxy tetralone. The condensation of this and similarly constituted tetralones with nitroso dimethylaniline followed by hydrolysis to naphthaquinones is the general procedure under experimental investigation.

Tetralone chemistry has received some attention in another direction. Methyl 4-keto-1, 2, 3, 4-tetrahydro-2-naphthoate gave the amide on shaking with ammonia, and the hydrazidehydrazone by treatment with hydrazine hydrate. The oxime also gave the oxime hydrazide. The Hofmann degradation of the amide and the Curtius degradation of the hydrazide gave interesting results. The only product that could be isolated was 1-naphthol. The degradation of the oxime hydrazide also gave the same result. The tetralone oxime afforded the p-toluene sulphonic ester in alkaline medium. The Neber rearrangement of this ester gave the amino ketone in very poor yield. Worse still the free base proved to be too unstable to be of use in synthetic work.

The preparation of certain compounds with structures less complicated than those of the steroid hormones, but having many

of their structural features has been undertaken. The intermediate required for the preparation of such compounds is 1, 5-dioxo-7a-methyl-2, 3, 5, 6, 7, 7a-hexahydro indene, which has been synthesized by an improved method involving the reaction of 2-methyl-1, 3-cyclopentanedione with 1-dimethylamino-3-butanone. Work is in progress to introduce the characteristic hydroxy acetone side chain of adrenal cortical hormones via the 1-oxo group. Similar analogues are also proposed to be prepared from 1, 6-dioxo-8a-methyl-1, 2, 3, 4, 6, 7, 8, 8a-octahydronaphthalene.

Experiments have been carried out to obtain direct chemical evidence for the non-planer structures of cyclohexanone, cycloheptanone and fluorenone. If these cyclonones exist in non-planar forms, it was considered likely that their carboxymethoximes might be capable of resolution. The carboxymethoximes of cyclohexanone and cycloheptanone formed only homogeneous double salts with L-brucine which could not be separated into diastereoisomeric forms. In the case of fluorenone carboxymethoxime, two crops of the brucine double salt, differing in rotation were obtained; these however regenerated the parent body of little rotation on decomposition with acid. Rapid interconversions of the non-planar forms are probably responsible for the failure of the attempts at resolution.

A few years back Dr. K. N. Menon and his collaborators worked out a method of estimating experimentally the glyceride composition of fats and oils. The method consists in acetone permanganate oxidation, fractional extraction of the azealoglycerides, finding the saponification value and computing the quantities. This method became essential as laboratories could not afford the cost involved in low temperature fractional crystallisation employed at Liverpool. The method evolved by Dr. K. N. Menon and collaborators found acceptance by workers in the field. One draw-back in the method is the uncertainty that no hydrolysis actually occurs during acetone-permanganate oxidation arising from the potassium salt formed. To lessen this possibility, periodical addition of small quantities of acetic acid was resorted to by Dr. A. R. S. Kartha, one of the collaborators of Dr. K. N. Menon. It is not certain that even this refinement is absolutely free from objection. A method has to be evolved, one which can be employed even in an ordinary college laboratory equipped only to teach to the B.Sc. level, which avoids the presence of alkali in any form during oxidation. Another great desirability is to have a cheap reagent to effect the cleavage of the glycol, formed as

the first stage of the oxidation, in a neutral medium. In an investigation on petroselinic acid, oxidation with peracetic acid or performic acid was found to be very effective in obtaining 6 : 7-dihydroxy stearic acid. Preliminary examination of per-acid oxidation of natural fats is encouraging. Before pursuing the problem to a further stage of development, it became important to develop a suitable reagent to cleave the glycol formed, working in a neutral medium. This has now been accomplished.

Oxidation of erucic, petroselenic and oleic acids with silver iodide dibenzoate in dry benzene resulted in the corresponding lower melting threo dihydroxy acids, whereas the use of benzene containing a small quantity of water gave mainly the corresponding higher melting erythro dihydroxy acids. It has been established that even traces of water brought about the inversion. An entirely new method of 1 : 2-glycol cleavage by the use of silver iodide dibenzoate has been established, and to the best knowledge of this laboratory, this constitutes the first record of 1 : 2-glycol cleavage by silver iodide dibenzoate; and constitutes one more elegant tool for the step-wise degradation of ethylenic compounds. Among the compounds that were tried out for this type of cleavage were:—

(a) 9 : 10-Dihydroxystearic acid yielding pelargonic aldehyde and azelaic semialdehyde.
(b) 13 : 14-Dihydroxy dehenic acid yielding pelargonic aldehyde and brassylic semialdehyde.
(c) 9 : 10 : 12-Trihydroxy stearic acid yielding β-hydroxy pelargonic aldehyde and azelaic semialdehyde.
(d) 6 : 7-Dihydroxy stearic acid yielding lauric alhehyde and adipic semialdehyde.
(e) Hydrobenzoin yielding benzaldehyde.
(f) α-Benzoyl glycerol yielding benzoyl glycolic aldehyde.

Degradation of the sequiterpene, longifolene, has been engaging our attention. Chromic acid oxidation in acetic acid medium has yielded, besides the known acid, and neutral fractions, a body of m.p. 131-132°, which gets thrown out when the sodium hydroxide extract of the oxidation product is saturated with carbondioxide. It yields a methyl ether of b.p. 144-146°/3 mm. and an ethyl ether of b.p. 152-155°/3mm. when treated in acetone solution in presence of anhydrous potassium carbonate with methyl iodide and ethyl iodide respectively. The methyl ether, although it distilled within a short boiling range, has started separating into a solid fraction and a liquid fraction on standing. Since this spontaneous separa-

tion of the methyl ether does not seem to be complete, further work on that is kept suspended.

The neutral fraction gave the known dione of m.p. 93-94° and a new product of m.p. 158-160° when the fraction distilling over at 200-230°/3 m.m. is fractionally crystallised from light petrol. The dione of m.p. 93-94° yields a dibasic acid of m.p. 225-227° on hydrogen peroxide oxidation in acetic acid medium at room temperature.

On the synthetic side in the terpene field, work is in progress to synthesize the bicyclic monoketone formed by the aldolisation of the primary oxidation product of patchouly alcohol. Camphor has been condensed with cyanacetic ester to yield the substituted ester with the double bond in the desired endo-cyclic position. The condensation of this with α-methyl-β-bromo-propionic ester is under investigation.

Work on vegetable drugs is also engaging our attention. Preliminary investigation has shown that *Cyclea burmani* yields a mixture of alkaloids that is amenable to fractionation. *Cryptolepis buchanami* has yielded a colourless, neutral product in fairly large amounts. The semi-solid residue from the petrol extract, on titura-tion with acetone, yields the solid product of low solubility in cold acetone. Extraction of bulk quantities of the drug is in progress.

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Govindan, T. K. 1956. Synthesis of an analogue of papavarine. *Curr. Sci.*, 25: 262

—— 1956. Heterocyclic Compounds. Part VII. Synthesis of 2-quinolyl benzimidazoles. *Proc. Indian Acad. Sci.* A, 44: 123-125

—— 1956. Heterocyclic Compounds. Part VIII. Synthesis of 1-quinolyl isoquinolines. *Proc. Indian Acad. Sci.*, A, 44: 126-129.

Indravathi, M. 1955. Heterocyclic Compounds. Part V. Compounds Structurally Related to the alkaloids evodiamine and rutaecarpine. *J. Madras Univ.* B, 25: 125-127.

Krishnan, M. 1955. Heterocyclic Compounds. Part VI. Synthesis of substituted Pyrido- (1, 2a)-pyrimidine-2-ones. *Proc. Indian Acad. Sci.*, A, 42: 289-291.

Menon, K. N. and Venkatasubramanian, T. A. 1951. Fatty Acids and Glyceride Composition of *Sesamum indicum*. *J. Madras Univ.*, B, 23: 272-281.

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Department of Physical Chemistry

I. *Photo-initiated free radical polymerization of vinyl Compounds in aqueous solution:*—

In the early thirties Haber and Weiss (1932, 1934) concluded that in the reaction between hydrogen peroxide and ferrous or ferric iron OH radicals were formed. Baxendale, Evans and Park (1946) have shown that OH radicals produced in the Haber-Weiss reaction lead to the initiation of polymerization of vinyl compounds in aqueous solution. Rabinowitch and Stockmayer (1942) interpreted the spectra of ferric ion-pair complexes in aqueous solutions as electron-transfer spectra. Evans and Uri (1949) have shown that atoms and free radicals produced by irradiation of ion-pair complexes lead to the polymerization of vinyl compounds in aqueous solution. Evans, Santappa and Uri (1951) have reported on the polymerization work using acrylonitrile, methyl methacrylate and methacrylic acid as monomers and ion-pair complexes of the type $Fe^{3+}X^{-}$ ($X^{-} = OH^{-}$, Cl^{-}, N_3^{-}, etc.) as photo-initiators. Santappa (1954) has extended this work and complete details of kinetics with azide, chloride and OH radicals and vinyl monomers have been reported. Subramanyan and Santappa (1956) have made use of ion-pair complexes $FeHctr^{+}$, $FeC_2O_4^{+}$ from ferric citrate and oxalate, aqueous solutions as photo-initiators in the polymerization of methyl methacrylate, methyl acrylate and acrylonitrile. Chaitanyan and Santappa (1956) have carried out similar investigations with methyl acrylate as the monomer and $Fe^{3+}OH^{-}$, $Fe^{3+}Cl^{-}$ as the initiators.

Light absorption fraction and electron transfer:—It is assumed that the absorption process is connected with the change.

$$Fe^{3+}X^{-} \xrightarrow[k_\varepsilon I]{h\upsilon} Fe^{2+}X$$

The energy difference between the complex $Fe^{3+}OH^{-}$ and the fully dissociated and hydrated state can be calculated from the thermodynamic data to be ~ 40KCal. The light absorption maximum on the other hand corresponds to ~ 90KCal. The difference is understandable on the basis of the Franck-Condon principle since no change in the internal nuclear distance will occur during the optical transition. This means that the internal nuclear distance and

the configuration of the solvated shell in $Fe^{2+}OH$ will be the same as that in the ion-pair $Fe^{3+}OH^-$. The system will, therefore, be in a non-equilibrium configuration and the difference of ~ 50KCal is to be attributed to the repulsion energy between the nuclei in these states. A dissociation of the complex $Fe^{2+}OH$ might, therefore, be expected. OH radicals thus produced lead to subsequent reactions such as the polymerization of vinyl compounds. The light absorption process and electron transfer process hold good for other complexes $Fe^{3+}Cl^-$, $Fe^{3+}N_3^-$, $Fe^{3+}Hctr^{2-}$ and $Fe^{3+}C_2O_4^{2-}$.

The reaction scheme: The following reaction scheme includes those reactions which are likely to occur:

(1) Light absorption process k_ε is the fraction of light absorbed by $Fe^{3+}X^-$)

$$Fe^{3+}X^- \xrightarrow{k_\varepsilon I} Fe^{2+}X$$

(2) Primary dark back reaction

$$Fe^{2+}X \xrightarrow{k_d} Fe^{3+}X^-$$

(3) Initiation of polymerization of monomer, M, by the primary product $Fe^{2+}X$

$$M + Fe^{2+}X \xrightarrow{k_i} Fe^{2+} + X - M -$$

(4) Separation of the primary product

$$Fe^{2+}X \xrightarrow{k_s} Fe^{2+} + X$$

(5) Secondary dark back reaction

$$Fe^{2+} + X \xrightarrow{k_o} Fe^{3+} + X^-$$

(6) Free radical initiation of polymerization

$$X + M \xrightarrow{k_i} X - M -$$

(7) Proporgation of polymerization

$$X - (M)_n - + M \xrightarrow{k_p} X - (M)_{\overline{n+1}}$$

(8) Termination of polymerization

(a) by disproportionation or by free radicals :

$$X-(M)_p-+X\xrightarrow{k'_t}X-(M)_p-X$$

(b) by recombination of active endings

$$X-(M)_p-+-(M)_q-X\xrightarrow{k_t}X-(M)_{p+q}-X$$

A 250-W high pressure mercury vapour lamp (BTH) was used as a light source which was rendered parallel by a quartz condenser lens and the parallel beam passed through a series of filters for purpose of isolation of monochromatic wavelengths 313, 365, 405, 435 mμ etc. A quartz reaction cell 46 mm. long, 50 mm. diameter) containing the deaerated system vinyl monomer-ion-pair in aqueous solution was placed in a thermostat at 25 to 30°C and irradiated by the monochromatic beam for an hour or two till *ca.* 10 to 15% conversion of the monomer took place. The variations in rate of monomer disappearance, -dm/dt (by weight of the polymer); the rate of ferrous ion production dFe^{2+}/dt (colorimetrically by o-o′ phenanthroline) and the chain lengths of the polymers, n, (viscometrically) were studied as a result of changes in (1) light absorption by the ion-pair, k_ε (by change of pH or ferric ion concentration) (2) light intensity, I (actinometrically), (3) monomer concentration (M), (4) quantum yield for ferrous ion production (γ) and (5) initially added ferrous iron and ferrous iron formed during the course of the reaction. Using stationary-state kinetics the reaction scheme would lead to

$$dFe^{2+}/dt=\frac{k_\varepsilon I}{k_d+k_s+k'_i M}$$

$$\left\{(k_i\,(M)+\frac{k_s k_i\,(M)}{k_o\,(Fe^{2+})+k_i\,(M)}\right\} \qquad (1)$$

Had the initiation of polymerization occurred mainly by the primary product $Fe^{2+}X$ it would have meant that the quantum yield would rise with the monomer concentration and could not reach a constant value below unity. This was not borne out by our experimental results. On the contrary the quantum yields reached constant values below unity and were practically independent of

the monomer concentrations for all the complexes studied. It was therefore assumed that $k'_i(M) \ll k_s$ and, therefore,

$$dFe^{2+}/dt = \frac{k_s k_\varepsilon I}{k_d + k_s} \left\{ \frac{k_i[M]}{k_o[Fe^{2+}] + k_i[M]} \right\} \tag{2}$$

$$\text{and } \gamma_{Fe^{2+}} = \frac{k_s}{k_d + k_s} \left\{ \frac{k_i[M]}{k_o[Fe^{2+}] + k_i[M]} \right\}$$

The maximum quantum yield would be $k_s/(k_s + k_d)$ (3)

The fact that the maximum values for quantum yields were reached even in the absence of monomers indicated that radicals interacted with impurities in the distilled water under those conditions. This aspect of the impurities in the system has been fully discussed by Santappa (1954) separately. The applicability of equation (2) to the experimental results has been tested. (1) dFe^{2+}/dt V_s k_ε yielded linear function in all cases. (2) dFe^{2+}/dt against ferrous produced in the reaction or initially added was shown by plotting $1/dFe^{2+}/dt$ Vs Fe^{2+} when linear plots were obtained and from the slopes of the plots ko/ki values have been evaluated. Plots of dFe^{2+}/dt against (M) were more or less flats for reasons cited above with all complexes except $Fe^{3+}N_3^-$ in which case $1/\gamma$ was plotted against $[1/M]$ and k_o/k_i was evaluated from the slopes. From intercepts of plots under (2), $k_s/k_d + k_s$ values evaluated confirmed the values of maximum quantum yields in all respects. (3) The influence of light intensity was seen by plotting $dFe^{2+}/dt \; \{1 + k_o[Fe^{2+}]/k_i[M]\}$ against I using k_o/k_i obtained under (2).

The scheme also leads to the following expressions for rate of monomer disappearance :

$$-dM/dt = (k_p/k_t^{1/2}) \quad (k_s k_\varepsilon I/k_d + k_s)^{1/2} [M] \tag{4}$$

and for the chain-length of the polymers :

$$n = 2(k_p/k_t^{1/2}) \quad (k_d + k_s/k_s k_\varepsilon I)^{1/2} [M] \tag{5}$$

For many of the initiators used linear function of $-dm/dt$ against (a) $I^{1/2}$ (b) $k_\varepsilon^{1/2}$ and (c) [M] were obtained. Had the termination occurred by disproportionation or by free radicals stationary state

kinetics would have led to the dependence of $[M]^{1/2}$ and independence of $I^{1/2}$ on $-dm/dt$. From plots under (a), (b) and (c) values of $k_p/k_t^{1/2}$ have been evaluated for all the monomers with all the initiators. From plots of (n) against (a) $I^{-1/2}$ (b) $k_\varepsilon^{-1/2}$ and (c) [M] also $k_p/k_t^{1/2}$ values have been evaluated. The work conclusively proved that initiation of polymerization was by the free radicals and termination was by combination.

II. *A spectrophotometric investigation of the complexes of ferric iron with oxalic and citric acids* :—

This investigation is connected with I above because a knowledge of the instability constants, molar extinction coefficients, conditions for the stability of the ion-pairs $Fe^{3+}Hctr^{2-}$ and $Fe^{3+}C_2O_4{}^{2-}$ is necessary before they are used as photo-initiators of polymerization. A systematic spectrophotometric investigation of these complexes in aqueous solution was, therefore, undertaken by Subramanyan and Santappa (1955, 1956). It was found that equimolar proportions of ferric iron and oxalic acids formed a complex with a characteristic maximum absorption at 290 mμ. From measurements of optical densities of 1 : 1 mixture at 290 mμ at pH = 1 and 0·7 it was found that the peak at 290 mμ became sharp with lowering of pH. The existence of a single complex was confirmed by measuring the optical densities of ferric nitrate + oxalic acid solutions in which their mole fractions varied from 0·2 to 0·8 at a total molar concentration of 10^{-3}M. The difference between the observed extinction and that calculated on the basis of no reaction between the components was plotted against $[Fe^{3+}]/[Fe^{3+}] + [ox]$. The sharp maxima at the ratio 0·5 over the whole wavelength range studied (280 — 400 mμ) showed conclusively that the only complex formed under these condition was that in which ferric ion and oxalic acid combined in equimolar ratios :—

$$Fe^{3+} + H_2C_2O_4 \underset{}{\overset{K_1}{\rightleftarrows}} Fe^{3+}(H_xC_2O_4)^- + (2-x)\,H^+ \qquad (6)$$

whence

$$\log K_1 - \log \frac{(FeH_xC_2O_4)^{(1+x)+}}{[Fe^{3+}]\,[ox]} = (2-x)\log H^+$$

The value of x and, therefore, the ionic state of the complex was obtained from the slope of the plot

$$\log \{ [FeH_xC_2O_4]^{(1+x)+}/[Fe^{3+}] [ox] \}$$

against $-\log H^+$. The slope obtained was 2 and therefore the formula of the complex was $Fe^{3+}C_2O_4{}^{2-}$. The product $[FeH_xC_2O_4]^{(1+x)+}/[Fe^{3+}] [ox]$ was evaluated by using ferric thiocynate coloured complex as an indicator for ferric ions at equilibrium and measuring the optical density 1 : 1 M Fe^{3+} : oxalic acid at pH = 0·7 and ionic strength (μ), 0·5 at 525 mμ at which all the species except $FeSCN^{++}$ have negligible absorption. Then K_1 at pH = 0·7 and $\mu = 0·2$ was evaluated as $5·182 \times 10^2$. From the total absorption at each wavelength and with known $(FeC_2O_4)^+$ it was possible to evaluate the extinctions due to the complex and construct ε V_s λ curve for $\lambda = 2600$ to 4200 Å. Similar investigations were carried out in case of complex formation between ferric ions and citric acid. The formula of the complex established was $Fe^{3+}HCtr^+$ and the equilibrium constant k_2 for for the formation of the complex at pH = 0·7 and $\mu = 0·2$ was 2·16

$$Fe^{3+} + H_3Ctr \xrightarrow{K_2} Fe^{3+}HCtr^{2-} + 2H^+$$

and the extinction curve between $\lambda = 3200$ to 4200 Å was also drawn. The spectrophotometric study of ferric oxalate and citrate association complexes was necessary to calculate k_ε, the fraction of light absorbed by the complex required for our studies on vinyl polymerization with these association complexes as photo initiators.

III. *Chain transfer reactions and the nature of initiation in the polymerization of styrene* :—

Santappa and Vaidyanathan (1955) have studied transfer reactions between polystyrene radicals and solvents like acetic acid, propionic acid, n-butanol, iso-butanol, tertiary butanol, diethyl ketone, etc. all at 60 and 70°C under uncatalysed as well as catalysed (benzoyl peroxide) conditions. By a study of variation of the reciprocal degree polymerization against the ratio solvent : monomer or (S/M) it was possible according to the equation

$$1/P_n = 1/P_o + C_s [S/M] \qquad (7)$$

to evaluate the transfer rate coefficient C_s which is k_{fs}/k_p, k_{fs} and k_p representing the specific rate constants for transfer of polystyrene radical with the solvent and for propogation respectively. During the course of these investigations certain interesting observations not reported so far were made. The overall rate often decreased more rapidly with increasing [S/M] than that accounted for by the normal decrease of monomer concentrations. The existence of a critical ratio [S/M] for each solvent beyond which polymerization was retarded and sometimes completely inhibited was noticed. The slackness of secondary initiation by solvent radicals was concluded.

Another interesting aspect that was investigated was to determine the mode of initiation of polymerization by the catalyst. Conflicting opinions were expressed on the subject—some contending the formation of a complex between the monomer and catalyst and others opined that the initiation step was a unimolecular or bimolecular reaction between the catalyst and the monomer. If it is an unimolecular initiation one needs to keep the ratio $[\text{Catalyst}]^{1/2}/[\text{Monomer}]$ or $[\text{Cat}^{1/2}/\text{M}]$ constant in a study of variation of $1/P_n$ against [S/M]. For a bimolecular initiation it is $[\text{Cat}/\text{M}]^{1/2}$ that should be kept constant. It is now well recognized that the initiation process is quite different from the foregoing views and it is given by $2k_{df}$ [cat), k_d is the specific rate constant for spontaneous decomposition of the catalyst, having a catalyst efficiency, f, which is the ratio, $k_a[M]/k_a[M] + k_b \cdot k_a$ and k_b are the rate constants for the reaction of primary radicals with the monomer and with themselves respectively and the expression for P_n would be

$$1/P_n = k_t^{1/2}(k_{df})^{1/2}[\text{Cat}]^{1/2}/k_p[M] + C_s[S/M] \qquad (8)$$

If $k_a[M] \gg k_b$, f is unity and, therefore$[\text{Cat}^{1/2}/\text{M}]$ needs to be kept constant; on the other hand if $k_b \ll k_a[M]$, $[\text{Cat}/\text{M}]^{1/2}$ must be kept constant in a study of $1/P_n$ Vs [S/M]. In other words it is possible to evaluate the relative importance of the primary radicals from the catalyst for initiation or recombination between themselves. In a study of polymerization of styrene in toluene at 80—100°C by several catalysts, it was found that initiation reaction of primary radicals was important for the catalysts benzoyl peroxide, methyl ethyl ketone peroxide and tertiary butyl hydroperoxide while the initiation and recombination reactions had comparable rates with ditertiary butyl peroxide as the catalyst.

IV. *Rates of Initiation and Chain Transfer Constants in the Polymerization of Methyl acrylate* :—

The liquid phase polymerization of methyl acrylate is of considerable interest in view of the fact that considerable differences were observed between the gas phase polymerization of this monomer and other acrylic monomers. The general nature of polymerization of methyl acrylate in bulk under a variety of conditions, evaluation of rates of initiation, the chain transfer constants for reactions between the growing polymer chain and monomer, catalyst, etc., have been studied by Mahadevan and Santappa (1955). An accurate study of bulk polymerization of methyl acrylate was rendered difficult by the setting in at the very early stages of polymerization, the phase of auto-acceleration which could, however, be considerably reduced by using a diluent like ethyl acetate and confining polymerizations to low conversions of c. ten per cent, 50 as well as 20 per cent of methyl acrylate (5.5 and 2.2 molar) in ethyl acetate were employed. With benozyl peroxide as a catalyst at 60°C it was found that the overall rate constant, $R_p/[Cat^{1/2} M]$ decreased nearly four fold when [M] decreased from 8.8 to 2.2 molar. By using 5.5 molar monomer in ethyl acetate and for conversions 1 to 10 per cent little variation in overall rate constant was observed and with 2.2 molar monomer, the variation was minimum which indicated that the phase of auto-acceleration was kept to the minimum. Catalysts, benzoyl peroxide, tertiary butylhydroperoxide, ditertiary butyl peroxide and methyl ethyl ketone peroxide have been used at temperatures 65-75°C. At sufficiently high concentrations of the catalysts, the catalysed polymerization was very much faster than pure thermal polymerizations so that the equation for the overall rate

$$R = k_p (k_d f \text{ cat})^{1/2}[M]/k_t^{1/2} = K[M][Cat]^{1/2} \qquad (9)$$

was generally obeyed. In all cases a regular variation of overall rates with $[\text{catalyst}]^{1/2}$ were observed. The intercepts of these plots indicated the extent of thermal rate plus rate due to auto-acceleration. The intercepts which were 10 to 15 per cent of the total overall rates with 5.5 molar monomer disappeared with 2.2 molar monomer. From the slopes of R Vs$[Cat]^{1/2}$ plots the K values have been evaluated.

The relationship between degree of polymerization (P_n) and overall rate, R, in the absence of a chain transferring solvent is best represented by the equations:

$$1/P_n = (k_t R/k_p^2[M]^2) + k_{fm}/k_p + (k_{fo}[Cat]/k_p[M]) \quad (10)$$

$$= (AR/[M]^2) + C_M + (C_{cat}[Cat]/[M]) \quad (11)$$

[Cat/M] will be equivalent to R^2/K^2M^3. With very high concentrations of the catalysts or at high overall rates with low concentrations of the catalysts a curvature in the plots $1/P_n$ Vs. R was noticed. This was evidently due to pronounced transfer of the growing radical with the catalyst. At low catalyst concentrations and conversions transfer with catalyst was relatively so unimportant that a fairly good determination of A might be obtained. The plots were straight at values of catalysed rates far exceeding thermal rates that the determination of A was considered fairly accurate. The accuracy of these values, however, depended on the relationships between degrees of polymerization and intrinsic viscosities of polymer solutions and on the limitations imposed upon evaluation from the graphs with lot of scattered points. With known values of K and A rates of initiation (R) were evaluated,

$$2K^2A = 2k_d f(1+x) = R_i(1+x)/[Cat] = R_i'/[Cat] \quad (12)$$

Plots of $(1/P_n) - AR$ Vs R^2/K^2M^3 or

plots of $(1/P_n - AR)$ Vs [Cat/M]

With all the catalysts were all linera and C_{cat} and C_m were evaluated from the slopes and intercepts of these plots. A comparison of the values of rates of initiation at 70°C. indicated that benzoyl peroxide, methyl ethyl ketone peroxide and tertiary butyl hydroperoxide were of the same order of reactivity, R_i being equal to $5 \times 10^{-5}\,sec^{-1}$. Ditertiary butyl peroxide appeared, however, to be nearly fifteen times weaker than benzoyl peroxide for initiation. With regard to C_{cat} values all the catalysts except ditertiary butyl peroxide indicated the same order of reacivity ($\sim 10^{-2}$). The C_m values ($\sim 10^{-5}$ to $\sim 10^{-6}$) were of expected orders. Activation energies for R_i' C_{cat} and C_M were evaluated. With known k_d values for the catalyst it was possible to evaluate the catalyst efficiencies. In all cases it was nearly unity. The independence of catalyst efficiency on temperature was also realized.

V. Methyl ethyl ketone peroxide as an initiator in vinyl polymerization:—

Methyl ethyl ketone peroxide (MEKP) has not been extensively employed as an initiator in vinyl polymerizations. Gopalan and Santappa (1956) have carried out a systematic investigation of kinetics of polymerization of methyl methacrylate and styrene in bulk as well as solution with MEKP as an initiator at 65-80°C. The solvents used for the purpose were benzene, toluene, methyl, ethyl ketone and ethyl acetate. Per cent conversion against time curves both in bulk and in solution passed through the origin indicating the absence of period induction and suitability of the catalyst for further studies of polymerization. Employing a hundred fold variation of concentration of MEKP the order of reaction with respect to the catalyst was studied. Plots of Rates vs. $[Cat]^{1/2}$ were all linera both in bulk and in solution. From the slopes of these plots K values (equation 9) have been evaluated. From studies of 1/Pn. vs. Rates both in bulk and solution it was possible to evaluate A values (equation 11) also. The values of activation energies for K as well as A have also been evaluated. As described under Section IV, the C_{cat}, C_m and R'_i values for styrene and methyl methacrylate bulk polymerization with MEKP have also been evaluated. Evaluation of these constants in solution was also possible. The A values obtained by plotting 1/Pn. vs. R/M^2 in solution at different monomer concentrations was used to plot $(1/Pn) — (AR/M^2)$ against (S/M) at constant [Cat/M]. From the slope and intercept of the linear plots were evaluated transfer coefficients for the solvent, C_s and C_M respectively. For the R'_i values in solution polymerization for these monomers have also been evaluated. The order of the reaction, overall rate, with respect to monomer concentration was evaluated as 1·5 by plots of log R vs. log M in bulk as well as in solution. It could, therefore, be described that the reaction was of the first order with respect to monomer concentration and the other one half might be explained as the catalyst efficiency 'f' being dependent on monomer concentration. The decomposition of MEKP was also studied in ethyl acetate. It was found to have a spontaneous decomposition independent of the type of the solvent as well as an induced decomposition in the presence of the solvents.

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Department of Geology and Geophysics

The Department of Geology and Geophysics started with the appointment of a Reader in May 1952. The Reader appointed is Dr. P. R. Jagapathy Naidu, Ph.D. (Basel), who had worked previously for twenty years in the University of Mysore and is aged 53.

A hall and a room had been allotted to the Department in the Alagappa Chettiar College of Technology Buildings. During the first year these were fitted with electric, water and gas supply. Indents placed for furniture, optical and chemical equipment were being executed during the second year. A Research Assistant, Sri S. Ramanathan, M.A., was appointed in September 1953, and also a few students were admitted for research. With a partial equipment available in the Department at the beginning of 1954, research commenced and with the addition of apparatus in subsequent years, the Department was well-set for optical and chemical investigation of rocks, minerals, and ores. Thirty-four research papers have been published during the last two years (Ref. Appendix). The general scheme of research, as is current in the Western countries and in India, has been followed. An area in the Madras State was selected for detailed mapping of rock formations and structures. Various representatives of the rock formations are collected, these are brought to the laboratory and modern optical chemical techniques are applied to a study of these specimens.

According to the second Five Year Plan, submitted to the University, five districts were chosen in the Madras State for detailed mapping. These are Chingleput, Salem, Coimbatore, North Arcot, and Tirunelveli districts. Areas, roughly each of 200 sq. miles, were assigned to students for careful mapping and the specimens collected from them have been investigated on modern techniques of research. The results are embodied in five theses submitted for the M.Sc. and Ph.D. Degrees of the University, and in the thirty-four papers published from this Department. The results are summarised below.

Babu, has published six papers and has submitted a thesis for the Ph.D. Degree of the Madras University. In the paper

entitled 'Migmatisation in Kattriguppe Quarry, Bangalore district, Mysore State' (J. Madras Univ., B, XXV, No. 2 129-146, 1955), he has given a map of the Kattriguppe Quarry and has reported analyses of rock specimens. He has applied the technique of Doris L. Reynolds (Mrs. Holmes) to the chemical transformation of the rock types. By observing the geochemical changes involved, he has established the culmination and depression of cafemic and minor constituents, and has shown that the trend of differentiation in this area has been from amphibolite to quartz-diorite. He holds that the effect of the geochemical changes has been to produce rocks of normal igneous series by the process of mechanical pulverisation and reciprocal reaction.

In the paper entitled 'A Calciferous Amphibole from a Xenolith in Granite' (J. Madras Univ., B, XXIV, No. 3, 307-313, 1954) he has reported the analysis of a hornblende from an amphibolite, occurring as a xenolith in granite of Kattriguppe, Bangalore district, and its optical characters. The Niggli values of the analysed mineral lie within the range of values given for common hornblendes. W,X,Y, and Z values of the analysed mineral are compared with Berman's classification of common hornblendes. These values of the analysed mineral lie between those of hornblende-edenite and Hastingsite. The values of (Na, k), Al, Fe^{111}, and ca are plotted on the miscibility diagram of Sundius. The plotted point lies midway between Pargasite and Edenite indicating that the amphibole is composed of the molecules of Pargasite and Edenite.

In the paper entitled 'Anorthite Content and the Twin-Laws of the Plagioclase Feldspars of Some Granites and Gneisses from the Mysore State' (Quartly. Jl. of G.M.M. Society of India, Vol. XXVII, No. 1, March 1955) he gives the anorthite content and twin-laws of the plagioclase feldspars of granites and gneisses collected from the southern parts of the Mysore state. Köhler values were determined for the Mysore feldspars. These are generally in agreement with low temperature values of Köhler. Cumulative diagrams are given for the anorthite content and for various complex and parallel laws observed in the series.

The Pericline twins occur as fine lamellae across the albite twins. The grains, therefore, show combined albite pericline twins. The maximum incidence is of albite and percline laws, and the least of the carlsbad and albite-carlsbad (2) albite-ala law is fairly

abundant (49). Albite-ala is as much characteristic of granites and gneisses as the albite and pericline laws. The albite-ala law is more evident in the granites (29) than in the gneisses (14).

In the paper entitled "The Heavy Accessories of Chamundi Granites and Gneisses," Mysore, Mysore State (J. Madras Univ., B, XXV, No. 3, 291-300, 1955) he deals with the heavy accessories of 'Chamundi Granites and Gneisses', their distribution and variation. The frequencies are estimated and represented after Evans, Hayman, Majeed (1934), and also after the manner of Stark and Barnes (1935). An attempt has been made to correlate these rocks with granites and gneisses of Cuddapah. From the study and comparison of the heavy accessories of these two suites of rocks we find, that while the Cuddapah granites are essentially hornblende granites and are trondhjemitic in character (Naidu, 1954), the Chamundi granites are chiefly mica-granites. Though most of the other heavy minerals are common between the two areas, garnet is absent in the Cuddapahs. The association of biotite-garnet places the Chamundi granites at a higher grade of metamorphism than the Cuddapah granites.

In the paper entitled 'Tectonic and structural Study of Chamundi Granites and Gneissic Environs, Mysore' (J. Madras Univ., B, XXVI, No. 1, 31-50, 1956) he deals with the tectonic and structural study of the Chamundi granites and their gneissic environs. A map embodying structural features such as mineral orientation, foliation planes and joints is prepared along lines enunciated by Hans Cloos (described by Balk, 1937). The field relations of the different rock types found in the area are summarized. Megafabric as well as petrofabric diagrams have been prepared. Since it is seen from the fabric study, that there is preferred orientation in all the diagrams of granites, gneisses and migmatites the rocks are regarded as tectonites.

Balasubrahmanyan, has published three papers and has submitted a thesis for the M.Sc. Degree on the Sankaridrug and associated rocks.

In the paper entitled 'The Association and Genesis of Wollastonite and Scapolite-bearing Rocks of Sankaridrug, Salem District' (J. Madras Univ., B, XXV, No. 2, 153-185, 1955) he has studied the wollastonite and scapolite-bearing rocks of Sankaridrug, the contact metamorphic assemblages developed in calc-bands and discussed in the light of Eskola's facies. The geological and tectonic

relationship of the anorthite-gneiss of Sittampundi to the calc-gneiss of Sankaridrug is suggested.

In the paper entitled 'Some Minerals from the Calc-Bands of Sankaridrug, Salem District' (J. Madras Univ., B, XXV, No. 3, 263-270) he deals with the chemistry of the minerals occurring in the main calc-band passing through Iveli, near Sankaridrug. The study includes the analyses of a pyroxene, a wollastonite and an amphibole.

In the paper entitled 'Tectonics of the Granites, Gneisses, and Migmatities of Sankaridrug' (J. Madras Univ., B, XXV, No. 3, 255-61, 1955) he has made a structural study of the Sankaridrug massifs, based on the field-technique originated by Hans Cloos.

The microfabric of the country rock and a migmatite is reported and it is held that the petrofabric diagrams are those of schistose and quartz-rich rocks.

Leelananda Rao has published six papers and submitted a thesis for the Ph.D. Degree on the 'Charnockite Series of the Type Area of Sir Thomas Holland'.

In the paper entitled 'Twins, Parallel Growths, Parting and Extinction Angles in Pyroxenes of Charnockites from the Type Area of Sir Thomas Holland' (J. Madras Univ., B, XXIV, No. 1, 53-60, 1954) he finds that optic axial plane is invariably parallel to the lamellae in orthopyroxenes and perpendicular to the lamellae in clinopyroxenes. The lamellae are parallel to (100) in both. Growths of the two pyroxenes parallel to (100) are also present. The so-called Herring-bone twins are really the result of the accidental growing together of two individuals. The composition face is irrational. The inclined extinction angles in orthopyroxenes are normal extinction angles theoretically possible in orthorhombic crystals.

In the paper entitled 'The Geology and Petrology of Pachaimalai' (J. Madras Univ., B, XXV, No. 1, 55-81, 1955) he has noted that the khondalitic suite of rocks are typically represented in Pachaimalai. Based on petro-chemical studies it is concluded that the parent rocks of the khondalite series are arkosic or micaceous-sandstones partly very rich in quartz. Hedenbergite-garnet-magnetite rock, occurring intimately associated with the khondalites, shows close similarity to the related rock types of Eulysites of Loch Duich, Rosshire described by Tilley (1936). Charnockites and

Enderbitic charnockites show intrusive relationship to the khondalites. Field characters suggest that garnetiferous granulite (Leptynite) is a reconstituted phase of khondalites. Dyke rocks show some interesting evidences of assimilation.

In the paper entitled 'Dyke Rocks of Pallavaram' (J. Madras Univ., B, XXIV, No. 2, 213-23, 1954), he finds that dolerite dykes intermediate in character between pyroxenites and augite-diorite dykes occur in Pallavaram. The average anorthite content of the plagioclase feldspars of the dykes is Ab_{45} An_{55} and all the types of twin-laws, normal, parallel and complex are displayed by them. Pyroxenes occur as both twinned and untwinned grains. The phenocryst pyroxenes show variation in 2V from + 50° to + 40° and the ground mass pyroxenes from +40° to +25°. There is no break in the values of 2V from +32° to +40° as suggested by Hess (1941). The dolerite dykes of Pallavaram closely resemble the Cuddapah dykes in essential mineralogical and petrological characters.

In the paper entitled 'Further Studies on Dyke Rocks of Pallavaram' (J. Madras Univ., B, XXV, No. 3, 323-39, 1955) he describes the structural, petrographical and petrochemical characteristics of the dykes of Pallavaram. Following the petrographical methods of Niggli, the author is driven to the conclusion that these dykes belong to pacific suite and their parent magma is Eucrite. As the dykes show interaction along the contact zones, the possibility of contamination of magma in giving rise to tholeitic types is not altogether ruled out.

In the paper entitled 'Charnockites and Associated Rock Types of the type Area of Sir Thomas Holland: Part I' (J. Madras Univ., B, XXVI, 93-115, 1956) he presents a detailed map of the 'Charnockite series' of the type area of Sir Thomas Holland. The structural elements have been evaluated and the mutual field relationships of the rock types indicated. The area consists of Psammitic, pelitic, semi-pelitic, calcareous and igneous members which had attained earlier the sillimanite grade of metamorphism. These metamorphosed rocks have been later subjected to a regressive metamorphism by the intrusion of the Charnockites ('acid member of the Charnockite series' of Sir Thomas Holland).

Naganna, C., (J. Madras Univ., B, XXVI, No. 1, 1-9, 1956) reports that dyke rocks of composition of noritic olivine dolerites and olivine dolerites occur around Davangere, Mysore state. The

plagioclases of these rocks are all twinned and the anorthite content in them ranges from 58 to 72 per cent. All types of twin-laws, normal, parallel, complex and interpenetration, are noticed. Of the mafic minerals olivine and both ortho- and clino-pyroxenes are found. Two specimens of these rocks, texturally different are chemically analysed and their petrochemistry discussed. The magma which has given rise to these two types is found to fit into 'Gabbroide magmen' of Niggli's magma types and lies in between 'eukritisch' and the next 'c-gabbroid' types, the difference in colour and texture in these rocks is found to be due to the different cooling history of these rocks. These rocks bear a close resemblance to the dyke rocks of Dodkanya (Mysore State) which have an ultrabasic and charnockitic geological setting.

Naidu, Reader of the Department has published four papers.

In Current Science, May 1955, No. 24, pages 154-155, he has outlined two methods of measurement of extinction angles in hornblendes which show strong absorption. In the first method he gives a stereographic procedure of locating the optic axial plane and therefrom the extinction angle. In the second method, he aplies the Biot-Fresnel law.

In Current Science, Feb. 1955, No. 24, pages 47-48, he reports interference figures in reflected polarized light of rock forming minerals, and suggests that the interference figures are due to scattering of light in some cases and penetration into the media in other cases.

In Current Science, December 1954, No. 23, pages 387-389, he reports various types of twins in the cordierites from the burnt rocks of Jharia and Raniganj coal fields, and also the optical and chemical characters of the cordierites. He regards the complex patterns of twins as functions of temperature.

In the *Indian Mining Journal,* Vol. 2, No. 1, pages 12-17, January 1954, he gives the first of a series of studies on the granites of Southern India. In this, the first series, he describes granites occurring between Gulburga in the Hyderabad State, and Tiruttani in the Madras State, along a distance of 600 miles. The chemical characters of the rocks, and the optical characters of the minerals contained in them are given. The granites vary from Trondhjamites to granodiorites, through leucogranites, granites and quartz diorites.

Nehru, has published four papers and has submitted a thesis for the M.Sc. Degree on 'The Tiruchengode Granites and Its Relationship to the Sittampundi Anorthosite'.

In the paper entitled 'Tectonics of the Granites and Gneisses of Tiruchengode' (J. Madras Univ., B, XXV, No. 3, 227-233, 1955) from a study of the poles of joints in stereographic projection he concludes that the Tiruchengode granite intruded as a dome. The petrofabric diagram of the C-axes of the quartzes of the granite and migmatite of this area correspond to Ia and IVi of the schematic diagrams of quartz axes as given by Fairbairn (1954). The conclusion is reached that the granites and migmatites have been once quartzites, which have been subjected to rheomorphism.

In the paper entitled 'A Pyroxene from Sittampundi, Salem Dt.' (J. Madras Univ., B, XXV, No. 2, 167-172, 1955) he has analysed a clino-pyroxene from Sittampundi and has determined its optical characters. Its characters are compared with the pyroxenes of Adirondack Anorthosite Series and he holds that the pyroxene crystallized from a magma rich in aluminium and calcium.

In the paper entitled 'Geology and Petrochemistry of the Anorthite-Gneiss and Associated Rocks of Sittampundi, Salem Dist.' (J. Madras Univ., B, XXV, No. 2, 173-188, 1955) he has given analyses of the anorthite-gneiss and the associated rocks of Sittampundi (Salem Dist.), and has compared them to similar rocks occurring in calc-bands of Sankaridrug. These two bands together form an anticline warped up by the intrusion of the granites of the area. The origin of the Anorthite gneiss is considered not similar to those of Anorthosites occurring elsewhere. The view is put forward that the Anorthosite complex of Sittampundi represents a metamorphic facies of the Eclogite, and pyroxene-hornfels (sub-facies—spinel-Diopside-Anorthite—Grossularite sub-facies) grades. Original impure calcareous (non-magnesian) sediments and pyroxenite peridotite intrusions are the units metamorphosed.

In the paper entitled 'Two Amphiboles from the Anorthite and Biotite Gneisses of Sittampundi, Salem Dist.' (J. Madras Univ., B, XXV, No. 1, 19-28, 1955) he gives the analyses of an amphibole from Anorthite gneiss and another from an adjoining Biotite-gneiss and has determined their optical characters. Their chemical and optical relationships to other analysed amphiboles are discussed, and the amphiboles are calciferous aluminous amphiboles. The nomenclature of calciferous amphiboles is reviewed.

Raghavan, has published three papers on the Jalarpet granite. In the first paper 'Heavy Mineral Suites in the Granite Rocks of Jalarpet' (J. Madras Univ., B, XXV, No. 2, pages 147-152, 1955) he records the heavy mineral residue of the granitic rocks of Jalarpet. The index figure of the heavy residue has been determined. It has been observed that the minerals are distributed uniformly with no striking change in colour or form. Apatite, sphene and epidote, however, are more abundant in the hornblende-bearing granite than in the Biotite-bearing types.

In the second paper 'Plagioclase Feldspars of Granites, Gneisses and Associated Rocks of Jalarpet' (J. Madras Univ., B. XXIV, No. 3, pages 341-346, 1954) he deals with the anorthite content and twin-laws of the plagioclase feldspars of granites and gneisses, collected from the Yelagari Hills, near Jalarpet Railway Station. From Tertsch's stereograms, the feldspars of the Jalarpet series, are inferred to belong to the low temperature series. Cumulative diagrams are given for the anorthite content and various twin laws, observed in the series.

The Pericline twin occurs as fine lamellae across the albite twins—the grains show the combined albite-pericline twins. Albite-ala and albite law are of the largest incidence (53) and (52) respectively. Manebach-ala and Manebach-akline are the least (3). Albite-ala is more evident in granites (54% of the total) than in gneisses (34% of the total).

In the third paper 'Bluish-green Hornblende from an Amphibolite of Jalarpet' (J. Madras Univ., B, XXIV, No. 2, pages 245-250, 1954) he reports that a hornblende was separated from an amphibolite in Bromoform and various dilutions of Clerici's solution. Its chemical composition and optical characters were determined. Therefrom it is concluded that it corresponds to amphiboles occurring in gabbros.

Ramanathan, the Research Assistant of the Department, has published six papers, and has submitted a thesis for the Ph.D. Degree 'On the Ultrabasic Rocks of Salem and Dodkanya and Their Relationship to the Charnockites Series.'

In the paper entitled 'Plagioclase Feldspars from Charnockites of Salem' (J. Madras Univ., B, XXIV, No. 2, pages 225-236, 1954) he has determined the twin-laws of the plagioclase feldspars of the Charnockites of Salem. The more abundant twin laws are compared in a histogram. The abundance of albite and Pericline twin-laws and

the greater representation of untwinned grains are factors in favour of assigning a metamorphic character to these charnockites (cf. Turner and Gorai). A check on the laws is afforded by Nikitin's and Berek's constructions and also by calculating Köhler and Tertsch values, which correspond mostly to the low temperature values of the Austrian authors. Cumulative diagrams of all the poles of association planes and of the poles of twinning planes of complex twins are presented, the former shows a large dispersion.

In the paper entitled 'Shonkinites from the Ultrabasic Areas of Salem' (J. Madras Univ., B, XXV, No. 3, pages 315-333, 1954), he reports the occurrence of potassic rocks, Shonkinites rather rare rock types in the world from the ultrabasic areas of Salem. Their chemical analyses and optical characters are reported. The petrogenesis of the rocks is discussed.

In the paper entitled 'Vogesites and Noritic Olivine Dolerites from Salem and Dodkanya' (J. Madras Univ., B, XXV, No. 1, pages 29-54, 1955) he has studied five dyke rocks, two from Salem and the rest from Dodkanya, Mysore. He has analysed the rocks and determined the optical characters of their minerals.

The dykes of Salem (Vogesites) seem to be related to a Shonkinitic magma while those of Mysore (Noritic olivine dolerites) are related to a gabbroid magma.

In the paper entitled 'On the Hypersthene-bearing Rocks of Salem—Part I' (J. Madras Univ., B, XXVI, No. 1, pages 117-159, 1956) he gives a geological map of the ultrabasics and hypersthene-bearing rocks of Salem and a brief account of the texture, mineralogy, and chemistry of the hypersthene-bearing rocks. The hypersthene-bearing rocks are found to be of more than one age. The petrogenesis of these rock types is indicated.

Researches on the geology of Chingleput District the Charnockites and basalts of Vellore, metamorphism in Gangavarpet (Madurai Dist.), the geology of Western Ghats near Nagercoil, the granitic rocks between Madras and Palghat and basalts of Chindawara and Gulburga are under progress.

APPENDIX

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Department of Mathematics

The history of this department, in a sense, also marks the history of a new era of mathematical study and research in our country. While vast new fields were being opened up and a better and deeper understanding of the older fields of the subject gained by such investigations in Europe during the last hundred years, it is only in the last two or three decades that a just appreciation of these new trends and methods came to be among mathematicians in our country. And in this process of expanding the horizons of Indian mathematics this department of Mathematics under the able and far-sighted guidance of Dr. R. Vaidanathaswamy has played a considerable role.

After doing distinguished work in geometry and theories of algebraic forms during his stay at Edinburgh and London, R. Vaidyanathaswamy returned with a Ph.D. from London and a D.Sc. from Edinburgh to occupy the post of Reader and Head of the newly formed department of Mathematics from 1927. But in the course of his twenty five years of service in the University Dr. Vaidyanthaswamy continuously extended his domain of interest and initiated a whole generation of students to the intricacies and beauties of many branches of mathematics. Subjects of current research in the West, like modern algebra, set-theory, theory of partial order, symbolic logic, and topology were introduced perhaps for the first time in any Indian University by Dr. Vaidyanathaswamy. Quite a few of the younger mathematicians of promise who have started their research career under the guidance of Dr. Vaidyanathaswamy will remember his enthusiasm and energy for the development of mathematics in our country. To him this department owes a considerable debt of gratitude for having raised it to a centre of active research and study in many fundamental branches of Mathematics.

It is, therefore, only fitting that in this year of the Centenary of the University, the University should be bringing out a volume of 'collected papers' published by Professor Vaidyanathaswamy.

The first three years Dr. Vaidyanathaswamy was engaged in preparing and publishing various papers on algebraic geometry and algebra, continuing his work in Scotland. The first ten or eleven papers (of those listed under his name in the bibliography attached)

were prepared during this period. From 1930 the Department was made permanent and Dr. Vaidyanathswamy confirmed as Reader. Among the earliest students in the department were Messrs. Audinarayanan, Nagabushnam and Krishnamurthy Rao. From even 1932 onwards Dr. Vaidyanathaswamy began arranging courses of lectures on various modern topics for the benefit of the research students.

S. S. Pillai, another great number theorist got the first D.Sc., degree from this University. Following him, B. Ramamurthy got his D.Sc., with a thesis on the 'Binary geometry of the rational norm curve.' V. Ganapathy Iyer got his D.Sc., with a thesis on 'Properties of integral functions with bounded values at a prescribed sequence of points'; A. Narasinga Rao with his thesis on 'Circle geometry' and S. Meenakshisundaram with a thesis on 'Fourier Ansatz and non-linear parabolic equations' followed, and P. Kesava Menon was the last to get his D.Sc. from this University with a thesis on 'Contributions to the Theory of Numbers.'

So geometry and function theory were the first fields of interest in the Department. Modern algebra came after this. Mr. T. Venkatarayudu, Miss. S. Pankajam, worked on groups and Boolean algebra for their M.Sc.; logic was also studied by Miss Pankajam and Mr. K. Chandrasekharan. In course of lectures during the years 1940 to 1945 Dr. Vaidyanathaswamy dealt with various current topics like symbolic logic, algebra of partial order, topology, set theory and so on. The work of the students of this time reflect these interests. K. Chandrasekharan with his work on Bessel summability, V. S. Krishnan with work on partially ordered sets and congruences for these, M. V. Subba Rao with studies of linear operators on function spaces and K. G. Ramanathan with his studies on finite Abelian groups got their M.Sc. degree then.

Ph.D. degrees were awarded by the University on the basis of theses to Mr. K. Chandrasekharan, Miss Suseela, Miss Padma, Mr. V. K. Balachandran, and Mr. M. V. Subba Rao. Messrs. V. S. Krishnan and K. G. Ramanathan took their doctorate degrees from external Universities (from Paris and Princeton respectively). Messrs. K. Chandrasekharan and S. Meenakshisundaram also went to the Princeton Institute for advanced study for post doctoral work.

Based on many courses of lectures that he had delivered in the Department, Dr. Vaidyanathaswamy published in 1947 his

treatise on set topology, wherein a special fature was the extensive use of lattice properties in topology, and a large collection of examples.

Geometry came back with Miss Suseela's work on Non-Desarguesian geometry and Miss Padma's work on Tensors and region complexes. Lattice theory was continued in the work of Mr. V. K. Balachandran, and linear spaces were studied by Messrs. M. V. Subba Rao and S. Sankaran. The former finished his Ph.D. thesis and submitted it to our University, while the latter went to complete his studies in Columbia University. Miss Padmavally did considerable work in set theory, in the study of cardinals, ordinals etc. C. S. Venkataraman followed Dr. P. Kesava Menon in the study of multiplicative functions and took a Ph.D., for this work.

From 1949 Dr. Vaidyanathaswamy was promoted Professor, and a lecturer, Dr. M. Venkataraman was also appointed. This helped to launch a new M.Sc. course of one year for post Honours candidates. Lectures were also kindly undertaken by the Professors of some of the neighbouring colleges. This M.Sc. course was organised in such a way as to make it easier for students coming from their Honours to gain the necessary extra background in modern branches of Mathematics to take up a research career. The first syllabus includes topology, function spaces, probability and quantum mechanics, the second comprises modern algebra, topology, group representations and quantum mechanics and the third treats of groups, lattices, rings, fields, set-topology and representation theory for various combinations of these basic structures. Syllabus 1 was used for three years, syllabus 2 for one year and the third syllabus has been used for the last four years.

The M.Sc. course has given many of the aspiring research workers a necessary background in basic branches of the subject, and has also provided the Department a ready source of trained students for research. The scholarships provided by the University, and more recently also by the Government of India have given the opportunity for research students to complete their studies effectively; for some to prepare their doctoral thesis for others to complete post-doctoral studies.

After the retirement of Professor Vaidyanathaswamy in 1952, the programme of work generally followed by him has been continued by his successor, Dr. V. S. Krishnan, who joined as Reader and Head of the Department from July 1952. The M.Sc. courses

are continued and provide trained candidates to take up research; and courses of lectures of two months or so each are given by the Reader and the Senior lecturer on various topics for the benefit of research students. Some of the topics so covered are: topics in topology, dimension theory, combinatorial topology, linear spaces, integration, number theory, measure theory and probability, uniformity, semi-uniform spaces, convergence and écart, homology theory, topological algebras, Lie groups, structure theory of semi-groups and other algebraic structures, etc.

These last years have seen the beginnings of a study of algebraic topology which in recent years has been expanding considerably in power and scope. The study of structural features of composite mathematical structures involving algebraic, topological and partial order structures has also been taken up.

A further welcome feature during these last few years has been the visit by eminent western Mathmaticians to our University; most of them had come as guest Professors to the Tata Institute of fundamental research at Bombay, and paid a visit to our University. Lectures by such visiting Professors were given by Prof. Maass from Heidelberg, Prof. Schwarz from Paris, Prof. Siegel and Prof. Deuring from Göttingen, Prof. Eichler from Germany, Prof. Ambrose from Massachusetts, etc.

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Department of Physics

The department of Physics was set up at the beginning of the academic year 1952-53. The department is engaged in research, both in experimental and theoretical physics, and conducts in addition a one year post-graduate (post B.Sc. Honours) course leading up to the master's degree in two subjects (a) X-ray and Crystallography and (b) Statistical Mechanics. The department has now grown very nearly to its full strength, as may be seen from Table I. The staff at present consists of the following: —

Professor: Dr. G. N. Ramachandran, M.A., M.Sc., Ph.D. (Cantab.), D.Sc., A.I.I.Sc., F.A.Sc.

Reader: Dr. Alladi Ramakrishnan, M.A., Ph.D. (Manch.), F.A.Sc.

Research Assistant: Sri S. Raman, B.Sc. (Hons.), M.Sc.

TABLE I

Number of students in the department of Physics during the period 1952-1956

Years	1952-53	53-54	54-55	55-56	56-57
Research					
for M.Sc. ..	1	3	4	1	1
for Ph.D. ..	2	2	5	9	11
Post-doctoral ..	—	1	1	—	—
Course					
X-rays and Cryst. ..	—	—	4	4	5
Stat. Mech. ..	—	—	4	—	4

The laboratory has been equipped mainly for X-ray and optical work, particularly for the study of biological structures by physical methods. This is being extended to include other physical and physico-chemical methods, so that the department may be in a position to undertake researches in all branches of biophysics in due course.

A summary of the main lines of research work being undertaken in the department and the important results obtained are given below:

BIOPHYSICS

1. *Structure of Proteins:*

A programme of research has been initiated on the structure of proteins, in particular on the Collagen group, which form a main sub-division of the fibrous proteins. Collagen is widely distributed, being the main component of skin and hide and of connective tissue, besides forming the main organic part of the skeletal system. The work on the structure of collagen was started in 1953. X-ray diffraction patterns of collagen fibres from various sources were obtained and a structure was proposed on their basis, which consisted of triple helical chains of amino acid residues stabilized by interchain hydrogen bonds (Ramachandran and Kartha, 1954). These are linked together to form cylindrical rods, which occur in a hexagonal array. Although the structure explains the features of infrared spectrum and chemical composition of collagen, it did not completely agree with the X-ray data for stretched collagen.

So a modified structure was proposed which was topologically very similar to the previous one (Ramachandran and Kartha, 1955a) and agreed with the essential requirements of the X-ray pattern (Ramachandran and Ambady, 1954). The three helical chains are now wound into a superhelix in the form of inter-twined coiled coils. Two hydrogen bonds could be satisfactorily formed for every three residues. The third carbonyl oxygen could be hydrogen bonded to the hydroxyl group of the hydroxyproline in the neighbouring rod. This explains, in a satisfactory way, the relationship between the stability of the collagen fibre and its hydroxyproline content. The Fourier transforms of this model was found to be in good agreement with X-ray diffraction data (Ramachandran and Kartha, 1955b). However, the structure was found to be sterically not very satisfactory involving a few short contacts. It could not also explain the naturally occurring sequence of the amino acid residues. The structure was, therefore, further revised, however, retaining the broad features of the previous structure. Insistence on the formation of more than one hydrogen bond in three residues was abandoned. An additional hydrogen bond was introduced through a water molecule (Ramachandran 1956).

The Fourier transform calculations showed that this gave better agreement with X-ray diffraction data. The spherical transform of this model has also been computed. This should theoretically correspond to the diffraction pattern of thermally shrunk collagen or gelatin. For in these cases the protofibrils remain intact, although they take a folded configuration and the X-ray diffraction can be expected to be a highly disoriented representation of the pattern of the normal state. The agreement between the spherical transform and the diffraction pattern of gelatin was found to be fairly satisfactory.

The absence of reflections like 110 in collagen is difficult to be explained when the coiled coil rods are arranged in a hexagonal array. This led to the proposal of a cylindrical lattice structure which explains in a natural way the absence of all reflections of the type *hko*, with both *h* and *k* non-zero. (Ramachandran and Sasisekharan, 1956). This model also naturally explained the equatorial long spacings observed in natural wet tendon by Cowan, North and Randall (1955).

On the experimental side, X-ray diffraction photographs were recorded for collagen fibres from various sources and under different conditions, wet and dry, stretched and unstretched, and treated with various reagents. Often it was found necessary to use inclined beam rotation technique, because this gave a greater angular range along the meridian and varying resolution along the layers. Charts and tables have been recently prepared to determine the ξ and ζ values from the film coordinates for the various tilts of the beam with respect to the oscillation axis.

The X-ray pattern of collagen, contrary to statements made by previous workers, has been found to exhibit significant changes when the fibres were chromium tanned. On the basis of the experimental results, some ideas have been developed regarding the mechanism of the fixation of chromium salts in collagen.

The influence of various lyotropic agents on collagen fibres has also been studied. It has been observed that a progressive alteration of the structure is brought about by the lyotropic agents although the original structure is regained by washing away the salts with distilled water. Some of the stages in the alterations mentioned above gave an X-ray pattern closely similar to elastin. The structure of elastin has also been studied and its structure is

also found to be based on a triple chain helical configuration closely similar to collagen.

Very recently, studies have been initiated on the keratin group of proteins, in particular on feather keratin.

2. *Crystallisation of Salts in Proteins:*

An interesting phenomenon, namely, the oriented crystallisation of inorganic salts has been observed with collagen fibres kept in suitable salt solutions and dried (Ramachandran and Ambady 1955). An important fact noticed with regard to the various salts which crystallised in collagen is that the unit cell dimension along the fibre axis is always very nearly a submultiple of 28·6 A or $2 \times 28{\cdot}6$A. In continuation of these observations, a detailed study of the calcification of collagen has been carried out. Collagen fibres when kept in a suspension of precipitated calcium phosphate gave an X-ray diffraction pattern closely similar to the pattern given by a section of normal bone (Ramachandran and Santhanam, 1956). The influence of the presence of other ions and pH on the deposition of apatite crystallites has also been investigated.

3. *X-ray Studies on Cuticles:*

As a result of X-ray studies made on the cuticles of arthropods, it was found that the epicuticle of scorpion contains chitin, a constituent which was formerly considered to be absent in the epicuticles of all arthropods (Krishnan, Ramachandran and Santhanan, 1955). The epicuticle in the case of scorpion and centipede was found to be composed of a protein-chitin complex, containing a large percentage of chitin. In other cases, no chitin was present in the epicuticle in agreement with the current ideas of the constitution of the epicuticle (Santhanam 1955).

CRYSTALLOGRAPHY AND CRYSTAL PHYSICS

1. *Crystal Structure Analysis:*

A new method called the Difference-Patterson method has been developed to solve crystal structures. The method was shown at first to work with simple crystals such as phthalocyanines and the isomorphous pair barium chlorate and barium bromate (Kartha and Ramachandran 1955). The method was also applied to a more complicated example and was shown to work well (Sasisekharan 1956). This method is being applied systematically to solve unknown structures of crystals in this laboratory.

As an adjunct to the structure determination of fibrous proteins, the crystal structures of some amino acids have been worked out. The crystal structure of DL-aspartic acid has been worked out (Amirthalingam and Ramachandran 1955) by a combination of trial and error methods making use of models with Patterson-projections along two axes.

The crystal structure of tyrosine hydrochloride and hydrobromide are being worked out by the D-P method. These are in the final stage of refinement. The structure determination of lysine hydrochloride is also in progress.

The crystal structure of some inorganic compounds such as potassium tellurate dihydrate and a new form of titanium carbide have also been determined.

During the course of the structure analysis, space group, unit cell and molecular weight determinations of various compounds have been undertaken (Kartha, 1954; Sundara Rao *et al.,* 1954; Srinivasan, 1956).

To save much of the labour of computing structure factors and Fourier transforms in the initial stages of structure determination, an apparatus was constructed for obtaining them optically. The apparatus is simpler than previous designs in that only one lens is used (Aravindakshan 1957).

Measuring the intensities of various reflections from crystals by a Geiger Counter, the absolute configuration of the atoms in sodium chlorate and glucosamine hydrochloride, have been determined, using the anomalous dispersion of the chlorine atoms for the CuKα radiation (Ramachandran and Chandrasekharan 1957).

The main features of the structure of the high temperature form of $KClO_3$ were worked out from the powder photograph. The structure was found to be a sort of mixture of the two twins of low $KClO_3$ (Lonappan and Ramachandran 1956).

2. *Thermal Expansion Studies*:

The work arose out of an attempt to determine the thermal expansion of the monoclinic crystal, potassium chlorate, with the idea of throwing some light on the interesting transformation that occurs after the transition point. As the experimental technique developed in this connection turned out to be very convenient and accurate, the method was used for determining the thermal ex-

pansion of other crystals having anionic groups of the type BO_3, viz., othorhombic KNO_3 and triclinic HBO_3.

From the transformation studies on $KClO_3$ it was observed that there occurs a change of symmetry from monoclinic to orthorhombic system above 250°C, and that the structures of the two modifications namely high $KClO_3$ and low $KClO_3$ must be closely related (Lonappan 1955a; Ramachandran and Lonappan 1957). The study of thermal expansion of KNO_3 for various ranges of temperature was made and the ellipsoid of expansion was determined (Lonappan 1955b). The measurements of thermal expansion showed in the case of orthoboric acid the occurrence of a negative expansion, the direction of which was found to be parallel to the shortest hydrogen bonds (Lonappan 1955c). Incidentally, this is the first time that the complete expansion tensor of a triclinic crystal has been determined by the X-ray methods.

3. *Perfection of Crystals*:

A Geiger Counter for counting X-rays together with the associated electronic equipment were constructed to study the texture of crystals. Using the Geiger Counter spectrometer and a polarising monochromator the degree of perfection of a number of crystals such as calcite, rock salt, quartz and lithium fluoride have been measured (Chandrasekharan, 1955a,b). The relative intensities of various reflections and also the variation of the intensities of a particular reflection with the degree of perfection are broadly in agreement with the expectations from the theory developed by Hirsch and Ramachandran (1950) (Chandrasekharan 1955b).

The theory of anti-reflections (Ramachandran and Kartha 1952) has been extended and the integrated values of the reflected and anti-reflected intensities have been obtained analytically for an internal reflection (Ramachandran 1954).

A paper has been published on the representation of any state of polarisation of a light beam (including partial polarisation). The Poincaré representation is used to discuss the theory of monochromatic depolariser (Ramachandran 1952).

THEORETICAL PHYSICS

1. *The Cascade Theory of Cosmic Ray Showers*:

Since the first formulation of the cascade theory of Bhabha and Heitler, considerable work has been done in this field which forms

one of the principal branches of the cosmic ray theory. The group here has been mainly concerned with the stochastic implications of cascade problems and seven papers have been published on this subject. Very recently, a new approach to the cascade theory has been suggested.

2. *Theory of Random Functions*:

Random functions have attracted the attention of pure mathematicians for a considerable time. But there seems to be a necessity for a physical approach which is more useful in the application of actual problems. In collaboration with the students, Ramakrishnan has developed a physical approach to stochastic processes and a phenomenological interpretation of integrals of random functions. Over fifteen papers have been published on this subject.

3. *Statistical Problems in Astrophysics*:

With the publication of five papers by Chandrasekhar and Munch on stellar statistics, a new field of application of stochastic methods has arisen in astrophysics. The methods developed in the department are quite suitable for the extension of stochastic ideas to such astrophysical problems. Seven papers have been published in the Astrophysical Journal on this subject.

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Department of Statistics

The work of the Department of Statistics in the University of Madras falls under three broad categories, namely, (i) teaching, (ii) conducting and guiding research and (iii) assisting in the designing of scientific experiments and planning investigations and in the analysis of collected data and interpretation of the results. The following pages contain a short historical account of the development of these functions and a review of the work that has been so far undertaken together with an appraisal of the aspects of study that are in progress. A list of publications prepared by the teachers and research scholars of this department, including the titles of theses accepted for research degrees, are appended to this account.

Historical Background :

The history associated with the origin and development of the Department of Statistics has influenced, to a great extent, the nature and content of the work undertaken in this Department. While Statistics was introduced as a subject for special study for the Honours degree course in Mathematics, even as early as 1920, it was introduced at the University level first only a decade later in the Department of Economics. In 1929 the Diploma Course in Economics, that was being conducted by the University, was revised and Statistical Methods was introduced as a subject for study. The new regulations that were brought into force from 1930 led to the creation of the post of Lecturer in Statistics in the Department of Economics from 1st July 1930. He was appointed to work under the direction of the Head of the Department and deliver lectures, conduct classes, and engage in research and assist in any other academic work relating to the Department of Economics. Thus Statistics was given a place first in the Department of Economics and this position was retained without any change for a decade.

It was decided in 1940 to institute a Diploma Course in Statistics at the University and also provide for the study of Statistics in B.A. and B.Sc. (Pass and Honours) courses from the next academic year. These changes presented the administrative difficulty of fixing the department of study to which Statistics should be assigned and this situation led to the creation of a separate department of study and research in Statistics in the faculty of Science. Thus, in 1941 the post of the Lecturer in Statistics was

separated from the Department of Economics and the lecturer constituted the new Department of Statistics. The Department of Statistics, thus constituted with a single lecturer, remained without any change till the end of 1952. In January 1953, the Lecturer, under the scheme of rotating Readerships, was promoted as Reader and as Professor from 1st January 1957. From July 1953 a post of Lecturer has been added, so that the Department at present has a Professor and a Lecturer. During this total period, three times the lecturer was either on leave or on deputation and in his absence part-time lecturers were appointed for the conduct of the Diploma classes. The details of the occupants of these posts are as follows: —

1. Mr. N. K. Adyanthayya, B.Sc. (Hons.), B.Sc. (Lond.), Lecturer in Statistics, Department of Economics (1–7–1930 to 1–7–1933).
2. Sri N. Sundararama Sastry, M.A., M.Sc., Ph.D. (Lond.), F.S.S., Lecturer in Statistics, Department of Economics (22–8–1934 to 31–10–1941), Lecturer and Head of the Department of Statistics (1–11–1941 to November 1943).
3. Sri D. V. Rajalakshman, M.A., M.Sc., Ph.D. (Manch.), F.S.S., Dip. Econ., Lecturer and Head of the Department of Statistics (18–7–1944 to 31–12–1952), Reader and Head of the Department of Statistics from 1-1-1953 to 31-12-1956, Professor from 1-1-1957 onwards; also Hon. Librarian, Departmental Libraries, 1953-54.
4. Sri G. S. Lingappaiah, M.Sc. (Mysore), Lecturer in Statistics (11-7-1953 onwards).

During the quinquennium, commencing from 1951, the facilities for research and teaching in the Department have been considerably improved by providing equipment, like calculators and tables, and by strengthening the library. Besides one University studentship the Government of India have allotted four scholarships for research and this year a research fellow on exchange from France has also been admitted. On the whole, seventeen research scholars worked in the Department and nine of them were awarded research degrees and two are awaiting the result of the theses submitted by them, while three others are continuing work in the Department.

Review of Work :

Ever since the creation of the post of Lecturer, emphasis has been placed on the teaching aspect of his duties. This was the

natural consequence of the circumstances under which the post was originally sanctioned. During the first decade, the teaching work was mainly for the Diploma Course in Economics. With the institution of the Diploma Course in Statistics and the formation of the Department of Statistics in 1941, the Lecturer was entrusted with the responsibility of conducting this course in addition to his usual teaching work in the Department of Economics. This change also added considerable amount of administrative work to him. In the same year, the Lecturer also commenced inter-collegiate lectures for students taking Mathematics Honours course with Statistics as a subject for special study. These lectures gradually became a part of the work of the Department and have been extended in recent years for the Statistics and Economics Honours courses also. During 1948-50, the Lecturer taught Statistical Methods applied to industry for the B.Sc. (Tech.) students. In 1952 he assisted in organizing a course in Statistical Quality Control under the U.N.T.A.A. scheme and also received the training. In addition to this the Reader also organized special lectures in Statistical Methods for scientific research for all research scholars. The addition of a Lecturer to the Department since July 1953 provided some relief in the teaching work of the Head of the Department for the Diploma Course in Statistics. Thus the teaching work of the Reader comprises of giving different inter-collegiate lectures and special lectures for the research scholars, besides the teaching work for the Diploma Courses in Statistics and Economics.

The second aspect of the work that was given prominence from the beginning was that of providing assistance in the academic work of the Department of Economics. This statistical assistance, which usually took the shape of analysis of collected data and interpretation of the results, was confined mainly to Economics during the early period. But, with the separate formation of the Department of Statistics, this assistance was gradually sought by workers in other departments of study and research. In this context, Statistics as a branch of scientific knowledge stands rather unique. The applications of the subject are found in every branch of experimental work that depends on quantitative measurements. This gradual recognition of the need for using Statistics in various branches of scientific study resulted in a phenomenal increase in the work of the Head of the Department. He has been giving assistance in designing experiments and planning investigations and in the analysis of collected data including interpretation of the results for research workers in various branches of studies. Though

this aspect forms a significant part of the work of the Head of the Department, this cannot take the shape of publication of this Department.

The third category of work, namely, conducting and guiding research, formed always an integral part of the activities of the Head of the Department. Research workers were being admitted ever since the post of Lecturer was created and these scholars from July 1953 have all been working under the guidance of the Reader. All of them possess normally good qualifications in Mathematics and in Statistical Methods. The list appended to this review contains most of the published articles and titles of theses accepted for research degrees arranged according to the alphabetical order by authors and relate to the studies undertaken by the staff members, Mr. Adyanthayya, Dr. Sastry, Dr. Rajalakshman, and the research students who worked under their guidance. Unpublished reports and papers awaiting publication are not included in the list. Mr. Lingappaiah who joined the Department as Lecturer in July 1953, has been mainly taking some of the classes for the Diploma Course in Statistics.

Various aspects of studies that have been undertaken by the Department can be broadly classified into two categories, methodological and applied. The close association of Statistics as a part of the Department of Economics for over a decade influenced considerably the choice of topics for research work. Applied problems that require collection and analysis of data and the interpretation of these results, particularly selected from the field of Economics, received greater emphasis. Even here the early investigations were based on data collected from the sector of Agricultural Economics. Besides a number of articles included in the appendix, the two booklets prepared by Dr. Sastry in collaboration with Dr. Thomas and the thesis of Dr. Rajalakshman accepted for the 'Gokhale Prize' belong to this branch of studies. Though emphasis continued to be on the applied work even after the formation of a separate Department of Statistics, there was a steady shift in the choice of subjects. Topics were selected from aspects of trade, industry, and prices. Number of papers published during the forties, including the thesis of Dr. Sastry accepted for the doctorate degree, were based on these studies. Equally important has been the gradual widening of the scope in the choice of topics for study to include various branches of knowledge, like Biology, Education and Demography, besides Economics. This expansion of work that resulted in a number of publications has been accentuated by the steady increase in the statistical assistance given to research workers in various branches of studies.

During the last decade these applied studies gradually shaped into two distinct branches of work. Current problems that involve statistical analysis of data and interpretation of the results form one branch. Under this category, choice of the topic for study can be from any branch of knowledge and the investigations usually lead to the preparation of a paper. This continues to be one of the aspects of work of the Department.

The other category of applied work related to empirical studies on observational data with the specific purpose of illustrating or providing verification of the results obtained on methodological problems. These studies often also help fundamental work on methodology. One important branch of studies undertaken in this category has been analysis of time-series. Commencing with the analysis of observational time-series, a number of investigations have been undertaken on the methodological aspects of the analysis and published as papers. This branch of theoretical work has been further pursued considering time-series as a particular aspect of stochastic processes. Some of the results in this branch of methodology have been included in the thesis of Dr. Rajalakshman. The study of some aspects of stochastsic processes is one of the important branches of methodological work that is being undertaken by the Department. In this emphasis is laid on the problems of specification and inference of suitable stochastic models along with the necessary empirical analysis of real or artificial data.

Work based on problems on methodology selected from the general branch of sampling distributions formed a part of the studies undertaken by the Department from the very beginning. Problems on correlation were taken first and later these studies extended to distributions associated with different test criteria. Study of samples drawn from normal and non-normal universes including some aspects of testing of statistical hypotheses continues to be a fundamental aspect on which work is in progress. Most of the results have been included as parts of theses submitted for research degrees and published as papers.

Another aspect of work recently introduced as a part of the activities of the Department is that of planning and conducting sample investigations. These have been designed to provide adequate practical experience and also serve as applied work on sampling techniques for research workers. The data collected will be analysed and published as applied work. With the growing importance of applications of Statistics, considerable expansion of all the activities detailed above can be expected in the Department.

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Department of Technology

The growth and development of the Alagappa Chettiar College of Technology is a fascinating history by itself. The question of instituting technological courses had been under consideration of the University of Madras ever since 1933, since it was conscious that there were needed researches in science that would have a more direct relation to human welfare which might also advance our basic knowledge of technology and that the trained technological personnel should be available to the industry in the Southern Region served generally by the University. This question was considered at several meetings of the Syndicate, but had to lie over for better days, for lack of proper finance. The department of Chemical Engineering was started in the year 1944 thanks to a generous donation of Dr. Alagappa Chettiar and subsequent State and Government of India aids to the College. In the year 1945, courses in Leather Technology and Textile Technology were also started. The scope and functions of the laboratories are concerned towards the achievement of the following aims:

1. To train personnel in the professions of Chemical Engineering, Textile Technology and Leather Technology.
2. To build up a centre of research for higher technological education and training.
3. To initiate research on problems connected with industrial needs of the region.
4. To build up a liaison relationship with existing chemical industry of the region and to help them in their expansion.

To fulfil the above duties the College has well equipped laboratories for analytical work and for instruction in the operation of pilot plants connected with specialized technologies. The departments have given technical advice to firms and industries on industrial projects and have carried out research investigations at bench and pilot plant level on fundamental and applied aspects of Chemical Technology. The years up to 1950 were mainly devoted to equipping the laboratories and integrating the courses. Since

then, however, more emphasis has been given to undertake research projects. The various phases of the research and development activities of the laboratories are described below.

Synthetics from Fats and Oils

A comprehensive review of the production of synthetic detergents from vegetable oil origin was prepared (Janardhan 1950a). Fractional crystallizations of commercial stearic acid from acetone and methyl alcohol, acetone and rectified spirit, and benzene and methyl alcohol binary mixtures were attempted with good results (Janardhan 1950b). Optimum conditions for ammoniation process for converting fatty acids into their corresponding nitriles were investigated (Janardhan 1950c). The nitriles thus prepared were converted into the corresponding amines by reduction at copper cathode (Janardhan 1953a) and the process was awarded a patent (44230 Indian Patent). Various conditions for dehydrating castor oil were tried in the presence of different catalysts like $NaHSO_4$, Silica gel, etc., and under reduced pressure (Kannayya & Janardhan 1950). Attempts were made to increase the unsaturation of dehydrated castor oil by halogenation and dehalogenation and the properties of the resulting resinous products were studied (Kannayya & Janardhan 1951).

Analytical Research

In a programme of development of analytical methods, various new techniques have been reported by the laboratory. The colorimetric method for the determination of copper employing rubeanic acid has been critically examined (Janardhan 1953). The colorimetric estimation of tin using phosphomolybdic acid has been developed (Subrahmanyan & Janardhan 1955). A summary of work carried out on estimation of tin by electrodeposition at controlled cathode potential from acid and alkaline solution has been done (Subrahmanyan & Janardhan 1955). A new and accurate method for estimation of germanium has been developed (Hamsath Ibrahim & Madhavan Nair 1956). The coulometric technique has been extended to a number of nonaqueous solvents and to mixtures of such solvents with water.

South Arcot Lignite Utilization

Investigations on the nature and properties of South Arcot Lignite included proximate analysis and determination of calorific

value, sulphur and nitrogen contents. The low temperature carbonisation assay was performed at different temperatures. The proximate analysis of the chars and the determination of their calorific value were also carried out (Subrahmanyan & Madhavan Nair 1954). A complete study of the low temperature tar, obtained from the lignite at 600°C, has been made. Besides a determination of the physical characteristics of the tar, the work comprised of distillation of tar into several fractions, alkali extraction of the phenols, followed by the fractionation of phenols and of the washed oil, and estimation of naphthalene, anthracene, phenol, and pyridine bases (Subrahmanyan & Madhavan Nair 1954). The germanium content of the lignite ash has been determined by gravimetric and polarographic methods (Subrahmanyan & Madhavan Nair 1955). Montan wax was extracted with solvents at different pressures. Preparation of high quality active carbons from lignite has also been studied under the influence of activating agents such as steam, zinc chloride, phosphoric acid, calcium chloride, etc., at temperatures varying from 500°C to 800°C. The adsorptive properties of the carbons obtained were quantitatively studied on different adsorbents like iodine, oxalic acid, methylene blue, malachite green, etc., and suitability of these carbons has been demonstrated for decolorising molasses, palm ghur and cane jaggery (Jagannadhaswamy & Madhavan Nair 1955). Aerial oxidation of lignite was done with fixed as well as fluidised beds and the best conditions for the maximum yield of humic acid have been worked out. The importance of humic acid as a soil conditioner in increasing the uptake of fertilizer has been established by an extensive series of pot culture experiments (Jagannadhaswamy & Madhavan Nair 1956).

Unit Operations and Process Research

Investigations on the kinetics of absorption of CO_2 by alkalis were completed (Chandrasekhar 1950). A study for developing a basic correlation between the power required for the transport of slurry was undertaken and design data were obtained (Poonen 1954). An investigation into the sedimentation of fine particles in a centrifugal field has given interesting results. The size analysis of ultrafine particles in the 1 to 5 micron range by the usual methods is a highly time consuming operation. A method of effecting this analysis using a super centrifuge has been developed in the laboratory (Raman 1955). A study of the nature of filtration, structure of filter cakes and the role of filter-aids in filtration was

made for evaluation of filtration technique (Subba Rau 1955). An investigation of the vapour liquid equilibria over ternary system involving acetic acid, water and salts has indicated that the vapour-equilibria for acetic acid-water system are highly influenced in the presence of salts (Venkataraman 1954). The design and fabrication of a direct fired firebrick lined rotary kiln was studied to evaluate the various factors influencing them (Jayaraman 1949). A design for a cylinder cap for use with leaky gas cylinders was developed (Jayaraman 1950). Description and operation of an experimental refrigeration unit as a heat pump has been discussed (Subba Rau & Govinda Rau 1955).

Potentialities of the development of cotton seed oil industry in India was stressed and economics of cotton seed crushing have been discussed (Laddha 1954). The various ginning processes used in India have also been discussed (Mohanty 1954). Vegetable oils of commerce have to be refined free from fatty acids before further processing. The usual method of effecting this is by adding alkali in sufficient quantity to neutralise the acids and removing the soap formed. Investigations were carried out to apply solvent extraction process to effect this separation and to discover suitable solvents to separate the fatty acids for the oils. In this connection, complete equilibrium and phase distribution data were obtained for peanut oil—oleic acid—acetic acid and peanut oil—oleic acid—furfural at 40°C (Venkataraman & Laddha 1955). Further investigations indicated that ethyl alcohol can be used as a selective solvent for extraction of oleic acid from groundnut oil—oleic acid solution (Venkataraman & Laddha 1955). The methyl esters obtained by methylation of castor oil were fractionated by means of liquid—liquid extraction technique to get a fraction richer in pure methyl ricinoleate. The study indicated that the solvents furfural and hexane can be used for such fractionation (Kasturirangan & Laddha 1955). In a study of the extraction of glycol from aqueous solution the ternary systems Glycol—n Butyl alcohol—water and Glycol—*iso*butyl alcohol—water were studied and equilibrium and tie line data have been obtained (Lakshminarasimhan, Gopalan & Laddha 1956).

The laboratories of the college are at present engaged with the problems of heat transfer in packed beds, extractive distillation techniques, liquid—liquid extraction studies and beneficiation of the naturally occurring ores in South India.

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Department of Zoology

The University Zoological Research Laboratory was started in 1927, largely due to the initiative and foresight of Sri K. Rammuni Menon, who was its first Director. The laboratory was accommodated in a single room in "Marine Villa" which was later demolished to give place to the present building. This was completed and occupied in 1933 when Prof. R. Gopala Iyer was appointed full time Director. From the inception of the laboratory, the main lines of research, have been of a marine biological character. In 1944, on the retirement of Prof. Gopala Iyer, Dr. N. K. Panikkar succeeded as Director. In November 1946 the present Director Dr. C. P. Gnanamuthu, took charge. In 1950 the staff of the Laboratory was added to by the sanction of the post of a reader and later the post of a lecturer. To these posts Dr. G. Krishnan and Dr. S. Krishnaswamy were appointed.

In 1948, a scheme for continuous supply of sea water in the laboratory was placed before the Government of India and was sanctioned in 1950 at a cost of Rs. 75,000/- this is nearing completion. Further generous grants obtained through the University Grants Commission enabled the equipment of the laboratory with more modern apparatus suitable for the pursuit of researches in animal physiology.

Contributions to Indian Zoology from the Department of Zoology University of Madras

I. *Plankton studies*: Though the "*Investigator*" had collected data regarding the physico-chemical and biological conditions of the Indian ocean and the Bay of Bengal, yet detailed observations regarding the plankton of the western part of the bay were first presented for the Madras waters in the form of a plankton calendar in 1932 (24, 167). In the subsequent years, plankton was collected nearly every day and data were collected from qualitative and quantitative analysis of plankton and from estimations of pH and salinity. During the last six years, sea water samples were estimated for silicates, phosphates, nitrates and oxygen concentration; and records of temperature, pH and salinity were maintained (168, 216, 217). Correlations between the fluctuations in the quantity of phytoplankton collected and the fluctuations in the amounts of the different plant nutrients were sought. The

hydrographical data gathered during last six years, showed that this area of the bay is as rich as any other sea; that the phytoplankton blooms do not show such marked seasons as in the temperate waters but nevertheless show marked peaks following the concentrations of nutrients; and that the numbers of copepods—which may be taken as the animal index of organic productivity—also show maxima, occurring close behind the diatom pulses. The seasonal fluctuations in temperature, oxygen content and concentrations of plant nutrients, shed light not only on the occurrence of coastal currents of a northerly and southerly character in September-February and March-August periods respectively but also the incidence of upwelling of bottom waters during May-July.

The organic productivity of temperate waters has been studied by several. But in India the rate of organic production was estimated for the first time at Madras and was found to be limited rather by a ceiling intensity of sunlight and the composition of phytoplankton than by the uniformly high temperature and the never-depleted-amounts of plant nutrients. It was found to range from 0·048 to 0·547 mg. of carbon per litre per day—which compares favourably with 0·02-0·41 and 0·00 to 0·88 mg. per litre per day obtained at Long Island sound and Georges Bank in the higher latitudes.

In the course of the plankton studies, the life histories of several coelenterates (174, 190, 192, 197, 201), polychaets (2, 4, 10, 116) molluscs (222), crustacea (27, 29, 163, 165), echinoids (8, 12), balanoglossids (184, 186, 189) and different species of fish have been described (7, 41, 176, 177, 179, 180). Several forms like *Sagitta bedoti* (264), *Cestum amphitrite* (15) and *Ctenoplana bengalensis* sp. (96A) were recorded for the first time in Indian waters or were new to science.

II. *Study of copepods*: Of the different groups of organisms which maintain the food cycle in the sea, the copepods which form 80% of the total surface plankton at Madras are rightly treated as "the animal pasturage of the sea". This group was singled out for intensive study since it has been exhaustively studied in other countries. In India, Sewell began this investigation as early as 1912 and has been followed up at Madras by Krishnaswamy who has identified and described over 132, 137, 138, 139) species of which seven are new to science. The life histories of 17 have been sketched (128, 129, 134). Their physiology is being studied. Of the weed-clinging Harpacticoid copepods, 90 species belonging to 43 different

genera have been idenitfied and described, 9 being new to science. About five families of Harpacticoids and Cyclopoids were found to have invaded and colonized the sandy beach at Madras. Of these minute, extremely modified copepods confined to the microscopic interstices between particles of sand, 19 species were described (141, 145, 147). All were established as new species since it was found that very litttle work has been done on the microfauna of this newly discovered environment and that these peculiar copepods are extremely limited in their dispersal and are specialized in their adaptations.

Several families of this extremely plastic order—the copepoda—have taken to a parasitic mode of life. Forms were collected from widely different hosts like sea anemones, prawns, crabs and fishes. About 24 new species were described (67, 69 to 71, 73 to 76, 78, to 85, 87, 88, 91, 93, 94) with notes on morphology, physiology and life histories.

Thus, this extremely diversified order of Crustacea has been studied intensively in relation to their different habitats and the papers published represent a definite contribution to our knowledge of the Crustacea so important from the point of view of fisheries.

III. *Study of helminth parasites*: The cestodes parasitic in the guts of different market fishes of other countries have been studied extensively. Of the Madras fishes, 74 species which act as hosts to larval and adult cestodes were listed (242, 243, 244, 265) and the parasites collected from these have been identified and described. The encysted and pleurocercoid stages of the larvae of nearly 23 species and the adults of over 54 species have been dealt with fully. A new family Monoporophyllidae and 17 new species have been described. 66 species of the trematodes, especially the Monogenea which damage the gills of their fish hosts, have been described. Of these nearly 23 are new to science (214, 215). Thus, it may be claimed that the taxonomic survey, which is a necessary prelude to experimental studies of their nutrition, respiration, their effect on the hosts, the factors responsible for their specificity, etc, has been completed.

Three species of Acanthocephala infesting Madras fishes were described and the life history of *Moniliformis moniliformis* whose larval life is spent in the cockroach and adult period in the domestic rat, was studied in detail by experimental infections of laboratory bred hosts.

IV. *Ecological studies*: The relation of animals to the different habitats in a tropical area marked by higher temperature average, absence of marked seasons, higher rate of bacterial decomposition, rapid depletion of oxygen and nutrients, is another field in which important contributions have been made. The brackish water areas of Adyar and Cooum have been studied with respect to the marine elements like the Actinians (190, 191, 193, 199) polychaets (1, 5), molluscs (221, 203, 204), Crustacea (169, 170) and fishes which breed there after the mouths of these rivers have been sand-barred and conditions of salinity, oxygen content and pH change. Notes on the breeding of the different groups of animals represented have been made and it was found that in common with other tropical fauna there is evidence of continuous and discontinuous reproductive activity probably accentuated by slight fluctuations in hydrographical conditions and in a few cases by lunar periodicity as well. Preliminary observations on the osmoregulatory powers of polychaets (125) and gastropods of these brackish waters have been made.

The microfauna, inhabiting the capillary waters of the twelve-feet wide intertidal zone of the sandy beach, have been studied intensively with reference to the ecology of this interstitial habitat. Like other well defined environments this is self-sufficient so far as food is concerned through the organic production by the diatoms, the derivation of particulate organic matter from the decay of forms cast ashore and rotation of nutrients maintained by bacterial agency. The compensation depth being only two inches from the surface and the oxygen content decreasing to 1.5 c.c. per litre at a depth of 10 inches, limit the biotope to this depth. The fact that this depth is not less than is found in sandy beaches of higher latitudes suggests that in spite of higher temperature and more rapid bacterial decomposition, increased oxygenation is maintained through active photosynthesis and by capillary currents sustained by more rapid evaporation. The specialized forms of copepods and nematodes — the major groups studied so far — their localized distribution and their being confined to particular levels of the different zones and their differing from other genera and species recorded from temperate areas are features of the department's contribution.

The community of sessile forms growing on harbour structures is of ecological interest. The growth of these tropical species appears to be continuous while their breeding varies from being limited to once or twice a year, to being continuous with a few

peaks of intensity or being uniformly continuous (205, 206). Within the harbour, the composition of the community differs at different stations though the numbers at all stations vary uniformly, being lowest in October-November. Studies on the settlement of sessile organisms showed that there is a regular succession of different communities (48) on the same test panels in the different months of the year and that salinity, depth of water, currents and the nature of substratum, influence the settlement of the larvae. The growth of *Modiolus striatulus, Bowerbankia* sp., *Cynthia* sp., and *Dasychone* sp. studied very closely in the different stations, and in the laboratory, revealed that the tropical rapidity of growth was associated with not temperature alone but also affected by other factors such as salinity, turbidity and the early incidence of sexual activity.

The factors responsible for the settlement of barnacle cyprids were studied experimentally in the field and in the laboratory. It was found that the formation of a primary film (51) of bacteria and algae is a prerequisite and that the gregarious attraction (50) of previously settled cyprids of same or related species favours settlement. The intensity of illumination, the speed of currents, the height of tide, the colour of substratum (52), the composition of the animal community in the area also influence the cyprids of different species (50), in a way clearly suggestive of the narrow zones of the natural habitat to which the adults are confined.

The study of the ecology of sedentary ascidians, crustacea and bivalves which foul and damage wooden craft and timber structures, was started eight years ago, earlier than anywhere else in India. 82 species of cirripedia which foul timber were collected and described (43-45, 53) 11 being new to science. Of the animals which bore into timber, 20 species of Teredines (33, 37), 6 species of pholads (54) and three species of amphipods and Isopods (241) were listed and described. Of these 17 were new to science. The life histories of several typical forms have been studied in detail and the data, accumulated regarding their capacity to digest cellulose, will aid in formulating measures to protect timber against these marine pests. During the last three years, the department has conducted extensive tests on different species of Indian timber in collaboration with the Forest Research Institute, Dehra Dun.

V. *Physiological and Histochemical Studies.*

It is well-known that tropical conditions favour an inward migration from the sea to the estuaries and backwaters. Such

migration involves special physiological adaptations, the most obvious being the development of osmoregulatory powers which condition their survival in media less saline than the sea. Naturally attention was directed to a study of the organs involved in osmoregulation. In the polycheats belonging to the family Nereidae, it was found that marked variations occur in the relative size and amount of blood supply of the nephridia in closely allied species inhabiting the sea, brackish and fresh water (117). In the stenohaline form *Perineris nuntia* the nephridia are small relative to the body size while in *Nereis chilkensis* which is able to withstand dilution of the external medium so as to enable them to thrive in brackish water, the size of the nephridium is comparatively larger and the blood supply to it more pronounced. These features are even more prominently seen in *Lycastis indica* which occur in fresh water. Similar studies were undertaken on the kidney of gastropods *Thais rudolphi, Murex tribulus, Cerethidia cingulatus, Vivipara varieta, Melania elegans* which have been taken from habitats of varied salinity conditions. Although the kidney shows similar structural features in all the above mentioned forms, in those living in brackish and freshwater, like *Vivipara* and *Cerithidia* special modifications occur in the form of extensions to the kidney containing renal filaments. These appear to be related to the habitat and the necessity for greater osmotic work in an external medium of low concentration. Another feature characteristic of these species is the variation in the musculature of the renal pore enabling a wider opening of the renal cavity. The significance of this feature of the forms living in media of low salinity conditions, may be to facilitate an increased outflow of water.

Detailed experimental studies on the relation between energy requirements as measured by the rate of oxygen consumption and the ability to survive in low salinity conditions involving osmotic work, have been carried out with reference to the prawn *Metapeneus monoceros.* The rate of oxygen consumption which increases when the animal is in hypotonic media attains a constancy after about a stay of sixteen hours in the medium. A study of the oxygen consumption in relation to temperature, pH, and oxygen content of the external medium showed that the rise of temperature increases the oxygen consumption but no direct effect was observable in regard to pH and oxygen content of the water within certain limits, but a marked decrease in the oxygen tension lessens the rate considerably.

Studies on the respiration of the common frog with reference to the mechanism of breathing and the role and significance of cutaneous respiration revealed interesting results. Contrary to the prevailing conception, it is shown that in addition to the movements of the buccal floor, the flanks play an important part in the respiratory movements recalling the respiratory mechanism of the reptiles. The above studies also showed that hitherto the importance of cutaneous respiration in frog has been somewhat exaggerated. The cutaneous respiration in frog appears to be only subsidiary to pulmonary respiration and is by itself inadequate to meet the respiratory needs of the animal.

A series of studies have been devoted to a study of the physiology of digestion in crustaceans and molluscs. In the prawn *Metapeneus monoceros* it was found that all the digestive enzymes are produced by the hepato pancreas capable of digesting carbohydrates, proteins and fats. The lipolytic enzyme digests lecithin, methyl acetate and olive oil, the proteolytic enzyme, fibrin, peptone and gelatine. Carbohydrates such as insulin, pentosans, raffinose are digested by the enzymes present. The ranges of pH and temperature within which the activity of these enzymes are maximum have also been determined. The importance of the digestive enzymes of the wood boring molluscs have been recognized and detailed studies on the sources and nature of these enzymes, their property and the factors influencing their activity have been made out with reference to the common wood boring teredinid of Madras, *Bankia indica* (32, 34). The digestive equipment of this species is peculiar in that it includes cellulose enabling it to live on wood. This obviously is an adaptation for their mode of life and habitat. An interesting feature is that in addition to cellulose, all the other enzymes for the digestion of fats, proteins and carbohydrates are present as in the allied groups like *Pecten* and *Ostrea*. The cellulose digesting enzymes are produced by the crystalline style and the digestive diverticula. The role of the enzymes of the crystalline style appears to be a preparatory one acting on large molecules reducing them to a simpler state. The cellulose in digestion is split up first into cellobiose which is further acted on by a cellobiase to complete the digestion.

Experimental studies were conducted on the influence of physical factors of the environment in the development of the ascidian *Polyclinum indicum*. An interesting result obtained is that the metamorphosis of the larvae of *P. indicum* is accelerated by

mechanical disturbances under laboratory conditions and it is suggested that this factor may have an influence in their natural habitat also.

In the last few years, histochemical studies have received much emphasis as the chemical constitution of an organ enables an understanding of its functional behaviour. The insect cuticle has been studied in considerable detail from the above point of view and some workers extended such studies to a few groups of arthropods suggesting a uniformity in all arthropods. It was, therefore, of interest to find that from studies carried out in the laboratory on the arachnid *Palamneus swammerdami,* the structure and composition of the cuticle differ very markedly from the conditions reported in insects and is unique among arthropods in containing sulphur containing amino acids and in the absence of tyrosine and phenolic substances (118, 120), These features are reflected in the mode of hardening of the cuticle. Although the similarity in this respect is suggested in the vertebrate keratin, it is clear that this is different from it for the X-ray diffraction pattern obtained with the epicuticle is very unlike that given by keratin. These features noted above have been recorded for the first time. It is considered that the arthropod epicuticle is a non-chitinous, lipoprotein layer. But in *Palamneous* it is found, from both histochemical tests and X-ray diffraction studies, to contain a proportion of chitin. Further studies revealed a similar occurrence of chitin in the epicuticle of the myriopod *Scolopendra subspinipes* which resembles *Palamneus* in the nature of the proteins and the mode of hardening. In the aberrant group Pycnogonida, the epicuticle presents features recalling those found in *Palamneus* but it is devoid of chitin. Along side of the above studies, attention was directed to strucure and mode of formation of the cuticle of crustaceans in which only few groups have hitherto been studied in detail. In the stomatopod *Squilla* the cuticular organization is similar to that of the decapod crustacea. From studies on the cuticle of *Penaeus* and *Squilla* it is noted that although the crustacean cuticle is fundamentally similar to that of insects, there is wide range of quantitative differences especially in regard to tanning, which appears to be unimportant in crustacea in which the prime cause of hardening is by calcification. The hardening of the cuticle at each moult is regulated and controlled by harmones produced by the neurosecretory centres in the eye stalk. These centres of secretion are the X organ and the sinus gland. A study of the histology and histogenesis of these organs has been made in the crab *Ocypode quadichaudii* and *Squilla holochista.* Other

neurosecretory centres in the central nervous system, are being investigated.

VI. *Anatomical and life history studies.*

From the very inception of the laboratory attention was directed to a study of the habitats, anatomy and life history of the more common organisms characteristic of the fauna of Madras. The anatomical studies include most of the invertebrate groups and fishes. Polychaets like *Marphysa* (5), *Glycera, Armandia, Dasychone,* crustacean *Neptunus* and *Emerita*; molluscs *Kalinga* (221), *Stiliger* (222), *Meretrix, Modiolus,* Echinoderms such as *Salmacis* (12), *Chondrocloea* (175), *Pentaceros,* and the teleost *Otolithus* (56) have been studied in detail. The anatomy of these types not only serve to fill a gap in our knowledge of Indian animals, but also showed by comparison with their allies in the temperate and colder regions, in what respects life under tropical conditions and the adaptations necessitated by such conditions, bring about modifications in anatomical features. This feature is more prominently seen in the life history studies of the animals of Madras. The study of the brackish water polychaetes like *Marphysa* (1) and *Diopatra* (116) revealed a marked alteration of the free-swimming phase in the life history and increased provision for the developing young. In *Marphysa,* the eggs are protected in gelatinous egg cases in which various stages of development are passed. The jelly serves for both protection against draught and as nutrient to the developing young. In *Diopatra* the eggs are of large size and richly laden with yolk. These are laid inside the tubes of the parent animals and the whole course of development is passed within the shelter of the tubes, and a free swimming larval phase is completely lost—similarly in the gastropod *Stiliger* (222), an abbreviated larval phase and rapid metamorphosis have been noted. An interesting observation in regard to the life history of the brackish water anemone *Phytocoetus gangeticus* is the occurrence of neoteny (194).

Life history studies of a number of marine types, whose larval stages are found in the plankton, have been made. The larvae of crustaceans, gastropods and coelenterates have been studied and the life history of principal species are now known. In this respect, detailed studies have been made of the fish eggs and larvae of Madras. Some of these have been successfully reared in the laboratory tanks and valuable information of the sequence of lar-

val stages, the food and food habits of the young fish have been gathered with reference to a number of species of common edible fish of Madras.

The life history studies have a special importance with reference to the fouling organisms which damage floating timber and the underwater structures. The life histories of molluscs and crustaceans which foul timber have been studied. Detailed knowledge is gained especially of the cirripedes of Madras harbour, their early larval stages, the metamorphosis, mode and conditions favouring settlement (46, 50, 51, 52).

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